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[54] **CLOTH PREPREG, PROCESS FOR PRODUCING THE SAME AND REINFORCING FABRIC**

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[21] Appl. No.: **88,635**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 24,957, Mar. 2, 1993, abandoned.

[51] Int. Cl.[6] **B32B 5/02**

[52] U.S. Cl. .... **428/229**; 139/36; 139/383 R; 8/147; 8/DIG. 16; 428/408; 428/902

[58] Field of Search .... 428/229; 8/147, DIG. 16; 139/36, 383 R

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[57] **ABSTRACT**

Disclosed is a reinforcing fabric comprising warps and woofs which are multifilament yarns made of carbon fibers, the widths W (mm) and finenesses D (d:denier) of the warp and woof satisfying the equation of:

$$W=k\cdot(D/\rho)^{5/9}$$

(wherein k represents 3.5×10^{-2} - 10.0×10^{-2} ($mm\cdot d^{-5/9}$) and ρ represents specific gravity of said carbon fibers), the woven fabric having a cover factor K_c of 90.0-99.8%. The warps and woofs are twisted to not more than 5 turns/m.

4 Claims, 6 Drawing Sheets

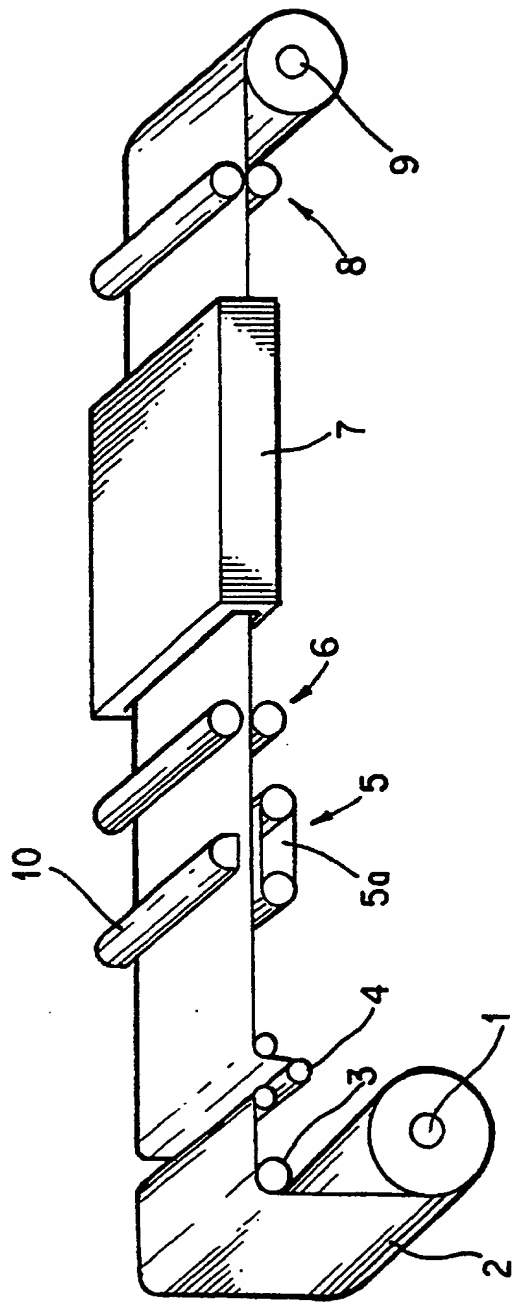

FIG. 1

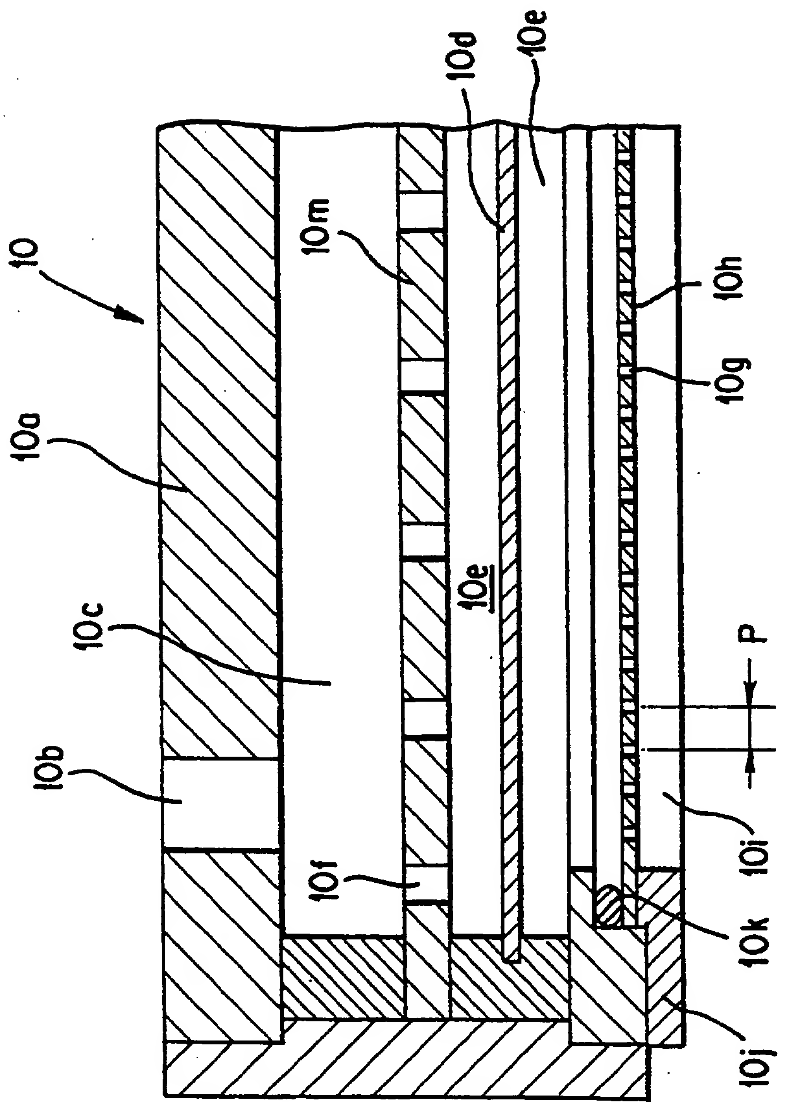

FIG. 2

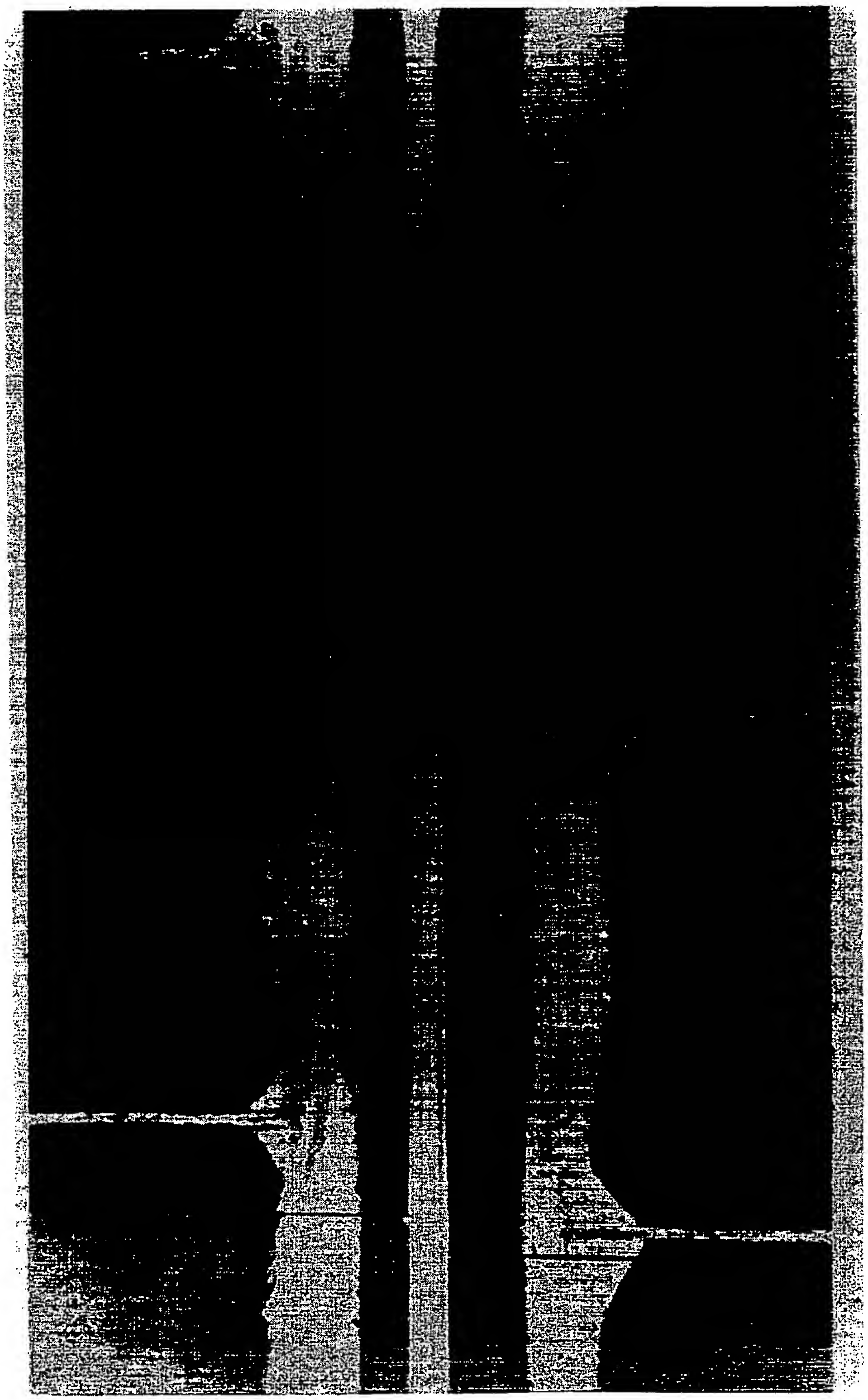

FIG. 3

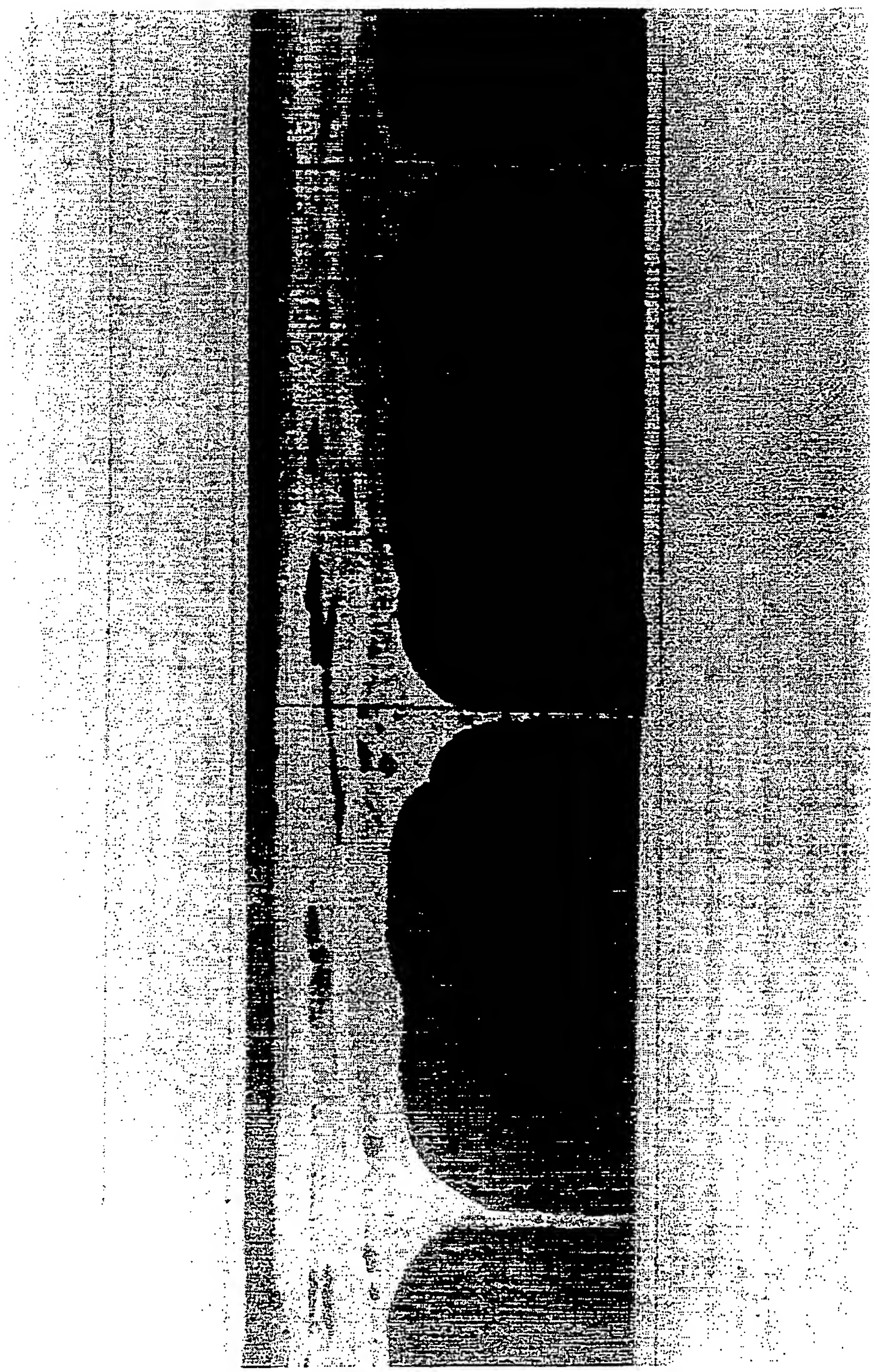

FIG.4

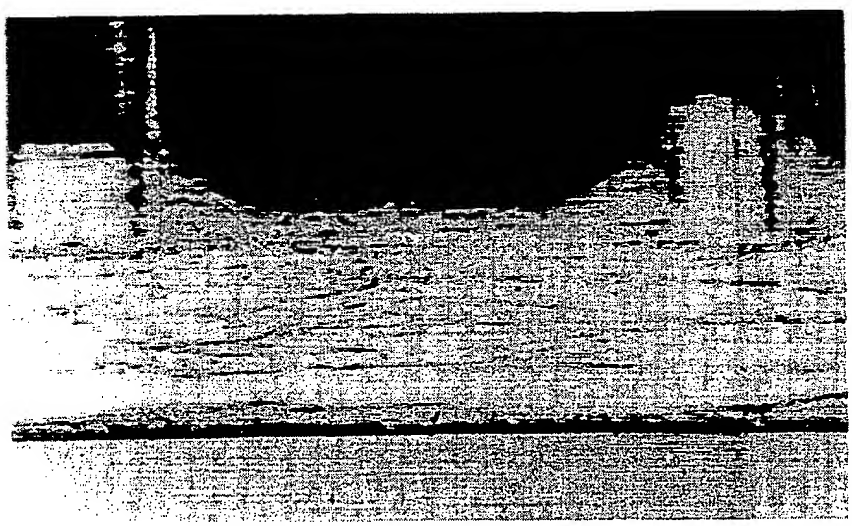

FIG.5

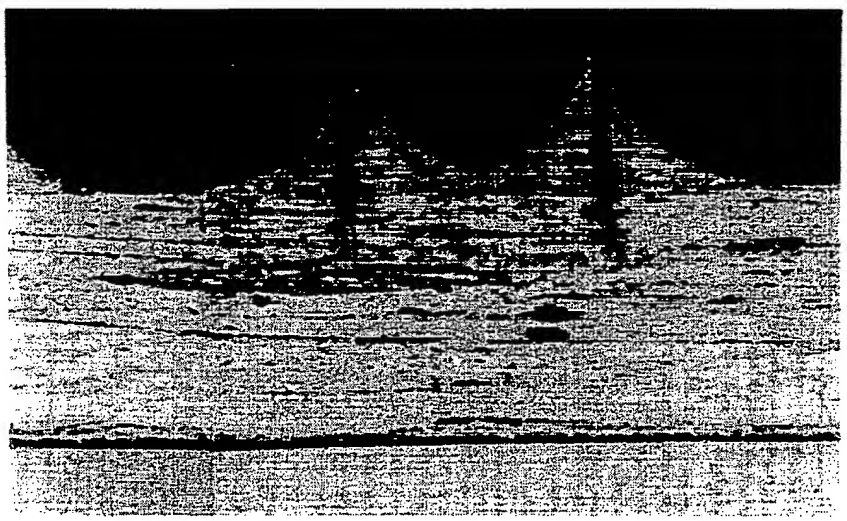

FIG. 6

CLOTH PREPREG, PROCESS FOR PRODUCING THE SAME AND REINFORCING FABRIC

CROSS REFERENCE TO THE RELATED APPLICATION

This is a continuation-in-part application of Ser. No. 08/024,957 filed-on Mar. 2, 1993, now abandoned.

BACKGROUND OF THE INVENTION

I. Field of the Invention

The present invention relates to a cloth prepreg and process for producing the same. More particularly, the present invention relates to a cloth prepreg which gives a fiber-reinforced plastic (hereinafter also referred to as "FRP") having high toughness and high modulus of elasticity as well as high thermal resistance, low water absorption and good solvent resistance, and which hardly forms pores in the FRP plate prepared by the so called honeycomb co-curing using the prepreg, and to a prepreg which gives an FRP having a good burn-through property.

II. Description of the Related Art

Epoxy resins are widely used in various industrial fields as molded articles, laminated articles, adhesives, sealants and the like exploiting their excellent mechanical properties, high chemical resistances and the like. Fiber-reinforced composite materials which have reinforcing fibers and matrix resins as indispensable constituents are used as structural materials of airplanes, automobiles and the like, and epoxy resins are widely used therein. Particularly, carbon fiber-reinforced plastics (CFRP) are conventionally used as structural materials of airplanes. To reduce the weight of the airplanes, honeycomb sandwich panel structure is often employed. The honeycomb sandwich panel structure is prepared by laying up prepregs on both sides of a honeycomb core made of aramide paper or the like (in some cases, via adhesive films), and the curing of the prepregs and the adhesion of prepregs to the honeycomb core are simultaneously carried out (this curing is called honeycomb co-curing). Thus, good co-curing properties are demanded for the prepregs.

It is also demanded that pores be not formed in the FRPs of the honeycomb sandwich panel. Since no pressure is applied to the regions of the prepregs on and under the inner space of the hexagonal cells in the honeycomb core, pores are likely to be formed in the interlayer zones and within one prepreg layer. If a molded plate having such pores are used to constitute a spoiler of an airplane, water is accumulated in the pores and when the airplanes flies at high altitude, the water is frozen to crack the skin (i.e., FRP of the sandwich panel). By repeating this, water comes to enter the honeycomb core and the physical properties of the panel is degraded, so that safe operation of the airplane is jeopardized. In other words, if the porosity of the FRPs are high, the reliability as a fiber-reinforced composite material is degraded.

There is the following prior art concerning the prepreg employing carbon fibers as reinforcing fibers and concerning matrix resins, which are designed to be used for the honeycomb co-curing.

Japanese Patent Publication (Kokoku) Nos. 63-30925 and 1-29814 disclose the following epoxy resin composition by which good direct adhesion between the prepregs and the honeycomb core and good composite properties of the cured plate as a surface material, especially, high interlayer shearing strength (ILSS) are attained. That is, as the epoxy resin, three types of epoxy resins, that is, bisphenol A type, novolak type and glycidylamine type are selected. The resin composition further comprises a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and a glycidylamine type epoxy resin, as well as nitrile rubber and dicyandiamide as a curing agent. The content of each component is made within a prescribed range by which the above-mentioned properties are stated to be attained. Japanese Patent Publication (Kokoku) No. 62-28167 discloses as a matrix resin suited for hybrid reinforcing fibers including carbon fibers and aromatic polyamide fibers, a composition comprising an epoxy resin, a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and an epoxy resin, and dicyandiamide, as well as liquid or semi-solid polyamide having amino group at its end. Japanese Laid-open Patent Application (Kokai) Nos. 58-82755, 58-83022 and 58-83031 disclose that by employing a composition containing a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and an epoxy resin, and both dicyandiamide and diaminodiphenylsulfone as curing agents, direct adhesion between the prepregs and the honeycomb core is promoted, especially at a high temperature.

Japanese Laid-open Patent Application (Kokai) Nos. 57-21427 and 57-21450 disclose that a prepreg prepared by impregnating into fibers a resin solution obtained by dissolving a composition containing an epoxy resin, a reaction product between liquid butadiene-acrylonitrile copolymer having carboxyl groups at both ends and an epoxy resin, nitrile rubber and a curing agent represented by dicyandiamide, in acetone-methyl Cellosolve mixed solvent or the like gives excellent adhesion strength, high impact strength and high bending strength to the honeycomb sandwich panel.

Japanese Laid-open Patent Application (Kokai) No. 57-49646 discloses that a prepreg employing a resin composition comprising an epoxy resin, nitrile rubber and a high molecular epoxy resin having a molecular weight of not less than 10,000 exhibits good direct adhesion to the honeycomb core, so that it gives high adhesion strength and high bending strength to the honeycomb sandwich panel. In the examples thereof, dicyandiamide is used as a curing agent and prepregs are prepared by dissolving the composition in acetone-methyl Cellosolve mixed solvent or the like.

Japanese Laid-open Patent Application (Kokai) No. 58-84825 discloses a prepreg in which an epoxy resin composition containing a bisphenol A type epoxy resin, an urethane-modified epoxy resin, an epoxy resin having N,N-diglycidylamino group, a brominated bisphenol A type epoxy resin and dicyandiamide is impregnated. It is described that the honeycomb sandwich panel employing this prepreg has excellent high heel resistance and high bending strength.

However, the above-mentioned prior art does not aim at reducing the porosity in the interlayer zones.

Further, if diaminodiphenyl sulfone alone is used as a curing agent which gives high thermal resistance, pores are much more easily formed in the interlayer zones than in cases where dicyandiamide is used as a curing agent, and this problem is very difficult to solve.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a prepreg which hardly forms pores in the cured FRP plates even when diaminodiphenylsulfone is used as a curing agent, which gives an FRP having high toughness and high modulus of elasticity as well as high thermal resistance, low water absorption and good solvent resistance, which has good tackiness and drapability and which gives an FRP having a good burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials.

Another object of the present invention is to provide a reinforcing woven fabric having an excellent uniformity of the opening, width-enlarging and flattening of the yarns, in which the bending of yarns at intersections is small so that breakage of the fibers is substantially avoided, which has an excellent surface smoothness so that the problems due to the uneven distribution of the carbon fibers can be avoided, and with which a carbon fiber-reinforced plastic (CFRP) having an excellent drapability, physical properties and reliability can be prepared.

The present invention provides a cloth prepreg comprising a resin composition including an epoxy resin, a curing agent and a solid rubber, and a woven fabric made of reinforcing fibers, the meshes of said woven fabric being crushed such that said prepreg has a cover factor K_p of 97–99.9%.

The present invention also provides a process of producing the cloth prepreg, comprising impregnating the resin composition containing a solid acrylonitrile-butadiene rubber having a functional group and a weakly cross-linked structure into the woven fabric in two steps, wherein in the first impregnation step, the resin composition is impregnated so as to attain a resin content W_R of 10–30%.

The present invention further provides a process of producing the cloth prepreg, comprising the step of impregnating a resin composition containing an epoxy resin, a curing agent and a solid acrylonitrile-butadiene rubber having a functional group and not having a cross-linked structure into a woven fabric having warps and woofs which are multifilament yarns made of carbon fibers, the widths W (mm) and finenesses D (d:denier) of said warps and woofs satisfying the equation of:

$$W=k\cdot(D/\rho)^{5/9}$$

(wherein k represents 3.5×10^{-2} - 10.0×10^{-2} ($mm\cdot d^{-5/9}$) and ρ represents specific gravity of said carbon fibers), said woven fabric having a cover factor K_c of 90.0–99.8%.

The present invention still further provides a reinforcing fabric comprising warps and woofs which are multifilament yarns made of carbon fibers, the widths W (mm) and finenesses D (d:denier) of said warp and woof satisfying the equation of:

$$W=k\cdot(D/\rho)^{5/9}$$

(wherein k represents 3.5×10^{-2} - 10.0×10^{-2} ($mm\cdot d^{-5/9}$) and ρ represents specific gravity of said carbon fibers), said woven fabric having a cover factor K_c of 90.0–99.8%.

The present invention still further provides a process for producing the reinforcing fabric of the present invention, comprising the step of treating said fabric with water jets from a nozzle apparatus having nozzle holes with an inner diameter of 0.05–0.5 mm and a pitch of not more than ⅓ of the warp pitch, the punching force of said water jets at the surface of said fabric being 0.1–3 gf per one water jet, the warps and woofs of said fabric being twisted to not more than 5 turns/m, the size of the mesh of said fabric being at least 1/5 of the width of said warps.

The present invention still further provides a prepreg comprising the above-described reinforcing fabric according to the present invention and a thermoplastic matrix resin.

The cloth prepreg of the present invention does not substantially forms pores in the cured FRP plates when subjected to honeycomb co-curing, and gives FRP having high toughness, high modulus of elasticity, as well as high thermal resistance, low water absorption and high solvent resistance. The prepreg also has good tackiness and drapability. Further, the cloth prepreg gives an FRP having a good burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials.

With the reinforcing fabric according to the present invention, the uniformity of opening, width-enlarging and flattening of the yarns is very high and the surface smoothness of the fabric is excellent. Therefore, uneven distribution of the carbon fibers when preparing a carbon fiber-reinforced plastic (CFRP), and in turn, generation of voids and portions containing too much resin can be substantially prevented. Further, the degree of bending of the yarns at intersections is small so that the problems due to the concentration of the stress can be avoided. Thus, by using the reinforcing fabric according to the present invention, CFRP having excellent drapability, physical properties and reliability can be obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view for explaining the production process of the reinforcing fabric according to the present invention;

FIG. 2 is a schematic cross-sectional view of the left half of a preferred embodiment of the nozzle apparatus which can be used in the process shown in FIG. 1;

FIG. 3 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Example 1 after polishing;

FIG. 4 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Comparative Example 1 after polishing;

FIG. 5 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Example 3 after polishing; and

FIG. 6 is a photomicrograph of a cross-section of the honeycomb sandwich panel prepared in Comparative Example 7 after polishing.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A component constituting the epoxy resin composition used in the present invention is an epoxy resin. Epoxy resin means a resin having not less than two epoxy groups on average per one molecule.

Preferred examples of the epoxy resins which are derived from amines include tetraglycidyl diaminodiphenylmethane, triglycidyl-p-aminophenol, triglycidyl-m-aminophenol and triglycidyl aminocresol. Among

these, tetraglycidyl diaminodiphenylmethane is especially preferred as a resin for composite material for a structural material of airplanes because it has excellent thermal resistance.

Preferred examples of the epoxy resins derived from phenols include bisphenol A type epoxy resins, bisphenol F type epoxy resins, bisphenol S type epoxy resins, phenol novolak type epoxy resins, cresol novolak type epoxy resins and resorcinol type epoxy resins. Since liquid bisphenol A type epoxy resins and bisphenol F type epoxy resins have low viscosities, they are suited for blending other epoxy resins and additives.

Preferred examples of the epoxy resins derived from compounds having carbon-carbon double bonds include alicyclic epoxy resins. Brominated epoxy resins obtained by brominating these alicyclic epoxy resins are also preferred since the water absorption of the resin is decreased and environment resistance is promoted.

The epoxy resin may be a mixture of two or more epoxy resins and may contain a mono-epoxy compound. The combination of a glycidylamine type epoxy resin and a glycidyl ether type epoxy resin is preferred because it simultaneously satisfies good thermal resistance, water resistance and processability.

In view of the balance of heat resistance, water resistance and processability, the combination of the following epoxy resins in the amounts shown is especially preferred.

Bisphenol A type epoxy resin 10–60 wt %
Brominated bisphenol A type epoxy resin 0–30 wt %
Tetraglycidyldiaminodiphenyl methane 10–40 wt %
Bisphenol F type epoxy resin 5–40 wt %

Another component constituting the epoxy resin composition used in the present invention is a curing agent. Any compound having active groups which can react with epoxy group may be employed as the curing agent. Compounds having amino groups, acid anhydride groups, azide groups and hydroxy groups may preferably be employed.

For example, dicyandiamide, various isomers of diaminodiphenyl sulfone, aminobenzoates, various acid anhydrides, phenol novolak resins and cresol novolak resins may be employed. Dicyandiamide is preferred because it gives long shelf-life of prepreg. If an aromatic diamine is used as a curing agent, cured epoxy resin having good thermal resistance can be obtained. In particular, various isomers of diaminodiphenyl sulfone are best preferred in the present invention since they give cured resins with good thermal resistance. Diaminodiphenyl sulfone may preferably be used in an amount such that the amount of its active hydrogen is 0.7–1.2 equivalent with respect to the amount of the epoxy groups of the epoxy resin. As the aminobenzoates, trimethyleneglycol-di-p-aminobenzoate and neopentylglycol-di-p-aminobenzoate may preferably be used. Although the resins obtained by using those curing agents have lower thermal resistances than those obtained by using diaminodiphenylsulfone, since they excel in tensile strength and toughness, they may be selected depending on the intended use. If an acid anhydride represented by phthalic anhydride is used as a curing agent, cured resin with good thermal resistance is obtained, and an epoxy resin composition having low viscosity and so having excellent processability can be obtained. A phenol novolak resin or a cresol novolak resin may also preferably be used as a curing agent since ether bonds having good hydrolysis resistance are introduced into the molecular chains, so that the water resistance of the cured resin is promoted.

Further, various curing catalysts may also be employed together with the above-mentioned curing agents. A representative example of the curing catalysts is monoethylamine complex of trifluoroboron. Cyanate resins (triazine resins) may also be employed together with the epoxy resin. In this case, a curing reaction takes place between the cyanate and the epoxy groups, so that a cured resin with low water absorption can be obtained.

The epoxy resin composition used in the present invention further comprises a solid rubber. Solid rubber herein means a rubber which does not have flowability at room temperature. The material of the rubber may be any elastomer.

By adding the solid rubber to the epoxy resin, a resin having high viscosity and high thixotropic property is obtained. During the fabrication, the matrix resin is in a quiescent state to which shearing force is not applied. The high thixotropic property means that the viscosity of the matrix resin is high in such a quiescent state. By virtue of this property of the resin, the formation of pores during the fabrication can be reduced. The rubber especially suited for giving high thixotropic property to the epoxy resin is solid acrylonitrile-butadiene rubber (acrylonitrile-butadiene rubber is hereinafter also referred to as "NBR") having a functional group and a weakly cross-linked structure. The term "weakly cross-linked" means that the rubber is cross-linked to such a degree that the rubber is swollen by a solvent but not dissolved in the solvent.

It is preferred that the solid rubber be three-dimensionally swollen and microdispersed in the epoxy resin so that it partially forms network, and that the solid rubber be not uniformly dissolved. Especially, the above-mentioned rubber having the weakly cross-linked structure is preferred since it always "phase-separated" from the non-cured state to the cured state, and is not uniformly dissolved at any time point. Although the degree of microdispersion of the solid rubber varies depending on the method of mixing and on the composition of the epoxy resin, the width of the rubber phase may preferably be 0.1–10 μm. If the dispersed phase is too small, the viscosity of the resin is unnecessarily decreased, and if the dispersed phase is too large, it hinders the impregnation to the reinforcing woven fabric so that it may be difficult to obtain a prepreg having uniform composition. In view of this, the width of the rubber phase may more preferably be 0.5–5 μm.

It should be noted that an epoxy resin composition having high thixotropic property may also be obtained by using a solid rubber which does not have a cross-linked structure, if an appropriate amount is used. This is also a preferred mode of the present invention.

Further, the solid rubber which does not have a cross-linked structure has relatively low viscosity, so that if a woven fabric of carbon fibers which satisfy the below-described specific equation and which have the below-described specific cover factor K_c is used as a reinforcing fabric, the object of the present invention may easily be attained. This is also a preferred mode of the present invention.

By the addition of the solid rubber, adhesiveness and flexibility of the resin composition are also promoted, so that the tackiness and drapability of the prepreg, which

are important characteristics for prepregs, are promoted.

The solid rubber used in the present invention may preferably have a functional group which reacts with the epoxy resin or the curing agent. By this, the solvent resistance and mechanical properties of the cured resin are promoted. Especially preferred functional group is carboxylic group.

It is also preferred to add polyether sulfones to the epoxy resin composition, since the viscosity of the resin composition as well as the tackiness and drapability of the prepreg may easily be controlled. In view of the compatibility with the epoxy resin, polyether sulfones having hydroxyl group at the terminals are preferred.

The content of the solid rubber in 100 parts by weight of the matrix resin composition may preferably be 3–12 parts by weight, more preferably 5–10 parts by weight, in view of preventing the too much decrease in the thermal resistance of the composite, and preventing the generation of pores due to the low viscosity of the resin. On the other hand, the content of the polyether sulfone in 100 parts by weight of the matrix resin composition may preferably be not more than 5 parts by weight, more preferably 1–4 parts by weight, in view of preventing prominent decrease in the tackiness and drapability of the prepreg.

In cases where the resin composition contains a solid rubber having a weakly cross-linked structure, the resin composition may preferably have a complex coefficient of viscosity $\eta_{0.02}$ measured at 80° C. under a vibration frequency of 0.02 Hz of not less than 5000 poise, more preferably not less than 20,000 poise, in view of keeping high viscosity in the quiescent state so as to reduce the porosity during the fabrication of the prepreg.

The complex coefficient of viscosity may be determined as follows using MR-3 Soliquid Meter commercially available from Rheology Co., Ltd.

That is, a plate-plate type (parallel plate type) system employing plates having a diameter of 1.798 cm and a gap between the plates of 0.5 mm is used. The measuring atmosphere is kept at 80° C. A sample is filled between the plates, and one of the plates is vibrated with a prescribed frequency to a amplitude of 1°. From the torque and phase difference generated by the vibration, the complex coefficient of viscosity is determined.

By measuring the complex coefficient of viscosity under the frequency from 0.02–2 Hz, the frequency dependence of the complex coefficient of viscosity can be determined.

In cases where the resin composition contains the solid rubber having a weakly cross-linked structure, it is preferred that the complex coefficient of viscosity η_2 of the resin composition measured at a frequency of 2 Hz and a complex coefficient of viscosity $\eta_{0.02}$ measured at 0.02 Hz satisfy the equation of

$$\log\eta_{0.02} - \log\eta_2 \geqq 0.5$$

in view of lowering the viscosity in the state that shearing force is applied, thereby assuring the easy coating of the resin film which tends to be difficult when the resin has a high viscosity.

In cases where the resin composition contains the solid rubber which does not have a cross-linked structure, in view of promoting impregnation property of the prepreg while keeping a good film coating property and while reducing the porosity, the resin composition may preferably have a complex coefficient of viscosity $\eta_{0.5}$ determined at 80° C. under a vibration frequency of 0.5 Hz during heating from 50° C. at a rate of 1.5° C./min (hereinafter referred to as "complex coefficient of viscosity $\eta_{0.5}$ at 80° C." for short) of 100–1500 poise, and have a minimum complex coefficient of viscosity η_{min} determined at 80° C. under a vibration frequency of 0.5 Hz during heating from 50° C. at a rate of 1.5° C./min of 50–300 poise.

In cases where the resin composition contains a solid rubber not having a cross-linked structure, it is preferred to employ a woven fabric made of carbon fibers which satisfy the equation of $W=k\cdot(D/\rho)^{5/9}$ and having a cover factor K_c of 90.0–99.8% as described below in detail, since especially advantageous effects are obtained.

The reinforcing fibers constituting the woven fabric may be any fiber which is used as a advanced composite material having good ~~thermal-resistance and tensile~~ strength. Examples of the fibers include carbon fibers, graphite fibers, aramide fibers, silicon carbide fibers, alumina fibers, boron fibers, tungsten-carbide fibers and glass fibers. Among these, carbon fibers and graphite fibers are especially preferred since they have high specific strength and high specific elastic modulus, and they largely contribute to the light weight of the prepreg.

Although any type of carbon fibers and graphite fibers may be employed depending on the intended use, high strength, high elongation carbon fibers having a tensile strength of not less than 350 kgf/mm² and a tensile elongation of not less than 1.5% are best preferred.

The reinforcing woven fabric made of the reinforcing fibers may be a conventional two-dimensional woven fabric. Biaxially woven fabrics having a fabric tissue in which warps and woofs cross at right angles, such as plane weaving, twill or satin are preferred.

In cases where the resin composition contains a solid rubber which does not have a cross-linked structure, in view of reducing the porosity, it is preferred to use a reinforcing woven fabric which has warps and woofs which are multifilament yarns made of carbon fibers, the widths W (mm) and finenesses D (d:denier) of the warps and woofs satisfying the equation of:

$$W=k\cdot(D/\rho)^{5/9}$$

(wherein k represents 3.5×10^{-2} - 10.0×10^{-2} ($mm\cdot d^{-5/9}$) and ρ represents specific gravity of the carbon fibers), and which has a cover factor K_c of 90.0–99.8%.

The cover factor K_c is the cover factor of the woven fabric, which relates to the size of the mesh of the woven fabric. The cover factor K_c may be determined as follows. That is, a region having an area S_1 is defined on a woven fabric. C_f which is defined by the equation of:

$$C_f=[(S_1-S_2)/S_1]\times100$$

is determined for optional **10** regions. The arithmetic average is defined as cover factor K_c. The larger the cover factor K_c, the more progressed the opening of the yarns, the enlargement of the width of the yarns and the flattening of the yarns, and the smaller the mesh of the woven fabric.

In order to avoid the formation of a region in the skin of the composite, in which carbon fibers do not exist, in

which resin is too much, or in which voids are contained, it seems that the cover factor K_c is preferably 100%, that is, the meshes are completely crushed. However, in such a woven fabric, the yarns are too much restrained each other and the freedom in the movement of the yarns are too small, so that the prepreg has poor drapability and wrinkles are likely to be formed. Thus, it is preferred to provide a very small clearance among the yarns so as to assure freedom in deforming. In view of the balance between the degree of opening, width-enlargement and flattening of the yarns and the drapability, the upper limit of the cover factor is preferably 99.8%. On the other hand, if the cover factor is less than 90%, although the drapability is good, the meshes are too large.

The concrete method for measuring the cover factor K_c of the woven fabric may be as follows:

First, using a stereoscopic microscope, e.g., stereomicroscope SMZ-10-1 commercially available from Nikon, a photograph of the surface of the fabric is taken while illuminating the back side of the fabric. Thus, in the photograph, the transmitted light pattern is shown, wherein the yarns are black and meshes are white. The intensity of the illumination light is so controlled that halation does not occur. In the examples hereinbelow described, the light from the double arm fiber commercially available from Nikon is used after reflected by an acryl plate. The magnification of the photograph is set to not less than 10 magnification so that 2–20 warps and woofs are contained, respectively. The obtained photograph is then photographed using a CDC (charge coupled device) camera and the image is then converted to digital data indicating white and black. The data are stored in a memory and then processed with an image processing apparatus to calculate the C_f according to the above-mentioned equation from the total area S_1 and the total area S_2 of the white portions. The above-mentioned procedure is repeated 10 times for different portions of the same fabric, and the arithmetic average is defined as cover factor K_c of the fabric. In the Examples later described, Personal Image Analyzing System LA-525 commercially available from Pierce Co., Ltd. was used as the CCD camera and the image processing apparatus. The range of the image-analyzed area was from the left most of portion of the left most warp to the right most portion of the right most woof, and from the upper most portion of the upper most woof to the lower most portion of the lower most woof. Within this range, 2–20 warps and woofs are included, respectively. In the digital data, intermediate portions (between white and black) is included between the yarns (black portion) and meshes (white portion). To clearly allocate the intermediate portions to the yarn portions or mesh portions, black tapes having a width of 6 mm were stuck on a transparent paper such that the tapes form a lattice. The lattice was normalized to have a cover factor of 75%. That is, the iris diaphragm of the CCD camera was set to 2.8, and the memory value of not more than 128 in the image analyzing system LA-525 was normalized to be yarn portion (In this system, the light and shade of the white and black is recorded as memory values of 0–255 grades.)

Such a woven fabric can be produced by, for example, as follows:

First, a woven fabric having warps and woofs made of multifilament yarns made of carbon fibers is produced by an ordinary weaving operation.

In view of the ease of weaving operation and of the uniformity of the dispersion of single fibers in a yarn after the below-described operation for opening, width-enlarging and flattening operation, the number of single fibers constituting a yarn may preferably be 3,000–30,000, and the fineness of the yarn may preferably be 1,200–40,000 denier. Although the number of fibers per yarn may be less than 3,000, in that case, the "k" in the above-described equation is 4.5×10^{-2} - 10.0×10^{-2} ($mm \cdot d^{-5/9}$).

The diameter of a single fiber may preferably be 5–10 μm. To make the opening, width-enlarging and flattening operation of the fibers easy and uniform, the number of twisting of the yarn may preferably be not more than 5 turns/m. Although from the view point of the opening, width-enlarging and flattening operation, yarns which are not twisted at all are preferred, weaving non-twisted yarns may be somewhat difficult. Thus, the yarns are preferably twisted to not less than 0 turns/m and not more than 5 turns/m.

Such a multifilament yarn may preferably be prepared by applying a sizing agent in an amount of 0.2–1.8% based on the weight of the yarns to twisted mutifilament yarns made of carbon fibers, drying the resultant, winding the dried yarns about a bobbin, and untwisting the yarns to not more than 5 turns/m. More particularly, twisted multifilament yarns made of precursor fibers are sintered to carbonize the fibers. Then a sizing agent is applied to the yarns and dried, followed by winding the yarns about a bobbin. Then the yarns are untwisted while rotating the bobbin. By this operation, due to the air resistance exerted to the yarns, a balloon is formed. If the amount of the applied sizing agent is 0.2–1.8% by weight, the sizing agent is peeled off by the friction with the air. As a result, the fibers become free from restraints by each other and the yarns are opened. The fabric made of such multifilament yarns can be subjected to a sufficient and uniform opening, width-enlarging and flattening operation even if the punching force of the water jet is small. That is, the opening, width-enlarging and flattening operation can be carried out under mild conditions. If an epoxy-based sizing agent is used, desizing is not necessary, so that the fabric after the opening, width-enlarging and flattening operation by water jet can be subjected to the step of forming prepreg or CFRP as it is. Conventional epoxy-based sizing agents may be used. Typical epoxy-based sizing agent may contain, in addition to an epoxy resin, polyethylene glycol, water-soluble polyurethane resin, polyvinyl formal resin, nonionic surfactant, anionic surfactant and/or a cationic surfactant. In cases where the epoxy-based sizing agent contains a water-soluble component or a surface active agent, the fabric may preferably be wetted by water or warm water since the sizing agent is swollen with water, so that the opening and width-enlarging of the fibers by the water jet may easily be attained.

In cases where the multifilament yarns made of the carbon fibers are used for preparing the woven fabric, to attain easy and uniform operation for opening, width-enlarging and flattening, it is preferred to make the clearances among the warps and woofs (i.e., the meshes) larger than those of the ordinary fabric. The degree thereof depends on the width of the yarns, but the width of the meshes is preferably at least 1/5 of the width of the warps. When the width of the warps is 1.5 mm, the best width of the meshes is about 0.5 mm.

The fabric tissue may preferably be plain weaving. It is best preferred that the warps and woofs have the same number of carbon fibers per yarn and have the same fineness, and that the weaving densities of the warps and woofs be the same.

The weight of the woven fabric per a unit area may optionally be selected. In view of ease and uniformity of the opening, width-enlarging and flattening operation, and in view of the shape-retaining ability and of the cover factor K_c, the weight of the woven fabric may preferably be 120–250 g/m^2, more preferably 140–195 g/m^2. This range of weight is especially preferred when the number of single fibers per yarn is 3,000. It should be noted that the weight per a unit area is not changed before and after the opening, width-enlarging and flattening operation of the yarns.

The woven fabric is then subjected to the operation for opening, width-enlarging and flattening the yarns constituting the warps and woofs. This may be carried out by continuously feeding the woven fabric in the direction of warps and treating the woven fabric with water jets from a plurality of nozzles arranged in the direction of the woofs.

For the ease of the operation for opening, width-enlarging and flattening the yarns constituting the warps and woofs, the diameter of the holes in the nozzles may preferably be 0.05–0.5 mm, the nozzle pitch may preferably be not more than ⅓ of the pitch of the woofs of the fabric, and the beating force per one water jet may preferably be 0.1–3 gf.

The above-described process will now be described referring to the drawings. As shown in FIG. **1**, a fabric **2** wound about a winding core **1** is introduced on a conveyor belt **5** having a metal mesh **5***a* as a conveyor belt through a rolling guide **3** and a dancing roller **4** which controls the tension of the fabric **2**. The fabric **2** is further introduced to a winding core **9** about which it is wound through a pair of dehydration rollers **6**, a drier **7** and nip rollers **8**. While continously moving the fabric as described above, water jets are applied to the fabric **2** on the conveyor **5** from a nozzle apparatus **10** located at a position 5–30 cm above the conveyor belt **5**. The water jets are applied to the fabric **2** at an angle of 90±20° with respect to the surface of the fabric **2**. By the punching force of the water jets, opening, width-enlarging and flattening of the yarns are carried out. The fabric after the operation is subjected to the dehydration rollers **6** by which water is squeezed out. The fabric **2** is then dried by the drier **7** and is wound about a winding core **9** through nip rollers **8**. The running speed of the fabric **2**, that is, the operation speed may preferably be, although it depends on the punching force of the water jet, 0.5–20 m/min. When the punching force is strong, the fabric can be treated at a high speed, and when the punching force is weak, the fabric can be treated at a low speed. The operation speed is more preferably 0.5–15 m/min. Needless to say, the direction of the warps is the longitudinal direction of the fabric. Therefore, the direction in which the fabric is running is the direction of the warps.

A schematic cross-sectional view of the nozzle apparatus **10** is shown in FIG. **2**. As shown in FIG. **2**, the nozzle apparatus **10** comprises a main body **10***a* in which a pressurized water inlet **10***b* is formed; an upper path **10***c* communicating to the pressurized water inlet **10***b*; a porous plate **10***d* by which lower path **10***e* is divided; an adjusting plate **10***m* having communication holes **10***f* which communicate the upper path **10***c* to the lower path **10***e*; and a nozzle plate **10***h* in which a number of nozzle holes **10***g* are aligned in a row at a pitch P. The nozzle plate **10***h* is attached to the main body **10***a* by a pressure-resistant plate **10***j* having an opening **10***i*. Reference number **10***k* denotes an O-ring for sealing. Although only a half of the nozzle apparatus is shown in FIG. **2**, another half has the symmetrical structure. Although the nozzle holes are aligned in a row in the embodiment shown in FIG. **2**, they may be arranged zigzag.

In operation, the nozzle apparatus **10** is arranged such that the row of the nozzle holes **10***g* is coincident with the direction of the woofs of the fabric **2** (i.e., the widthwise direction). Pressurized water is introduced from the pressurized water inlet **10***b* to the upper path **10***c* and then the water is introduced into the lower path after being adjusted by passing through the communication holes **10***f*. The water flow is further adjusted by the porous plate **10***d* so as to uniform the pressure and the water is jetted from the nozzle holes **10***g* of the nozzle plate **10***h* to form water jets. The nozzle apparatus **10** may preferably be shaken in the direction of the woofs of the fabric. The amplitude of the shaking may preferably be 1–5 times the pitch of the warps, and the period of shaking may preferably be 0.03–1 second.

The diameter of the nozzle holes of the nozzle apparatus is 0.05–0.5 mm. If the diameter is smaller than 0.05 mm, the quantity of water is not sufficient, so that sufficient energy for opening, width-enlarging and flattening the yarns cannot be obtained even if the punching force at the surface of the fabric is made strong. Further, the nozzle holes are likely clogged so that it is difficult to carry out stable operation. On the other hand, if the diameter is more than 0.5 mm, the quantity of water is too large and adjacent water jets interfere each other, so that the fibers constituting the yarns may be irregularly bent or the uniformity of the opening, width-enlarging and flattening of the yarns may be largely decreased.

The pitch of the nozzle holes is preferably not more than ⅓ of the pitch of the warps of the fabric. If the pitch is as large as more than ⅓ of the pitch of the warps, the unevenness of the energy distribution of the water jets on the surface of the fabric is too large, and in an extreme case, there is a warp to which water jet is not at all applied. As a result, the uniformity of the opening, width-enlarging and flattening of the yarns is largely decreased.

The punching force per one water jet at the surface of the fabric is adjusted to 0.1–3 gf. If the punching force is less than 0.1 gf, the punching force is too small so that sufficient energy required for the opening, width-enlarging and flattening operation cannot be obtained. On the other hand, if it is more than 3 gf, the punching force is too large, so that breakage of the fibers frequently occurs and the broken fibers become nappy. As a result, the uniformity of the opening, width-enlarging and flattening of the yarns is largely decreased. The punching force per water jet is preferably 0.1–1.5 gf, more preferably 0.3–1 gf. The punching force is determined as follows:

That is, an edge of a stainless steel plate with a thickness of 0.96 mm and a width of 40 mm, which has a strain gauge, is fixed. The portion of the steel plate, which is 150 mm away from the fixed end and 10 mm away from another end, is positioned at the surface of the fabric, and water jets are applied to this portion. As a result, the stainless steel plate is deformed by the

punching force by the water jets. The amount of the deformation is measured by the strain gauge to determine the force exerted to the stainless steel plate. The determined force is divided by the number of water jets applied to the steel plate. The obtained value is the punching force per one water jet.

By this operation, the warps and woofs may easily attain the widths and finenesses which satisfy the above-described equation of:

$$W=k\cdot(D/\rho)^{5/9}.$$

In the woven fabrics which satisfy this equation, the yarns are very uniformly opened, width-enlarged and flattened, and the bending at the intersectionsof warps and woofs is very small so that they excel in surface smoothness. It should be noted that "k" in the above-described equation relates to the degree and uniformity of the opening, width-enlarging and flattening of the yarns, and if the "k" is lower than the above-mentioned lower limit, the width-enlarging and flattening are not sufficiently progressed, so that the bending at the intersections of the yarns is large and the irregularity in the surface is also large. On the other hand, if the "k" is more than the above-described upper limit, the degree of opening of the yarns is uneven.

Among the woven fabrics described above, those in which the warps and woofs are made of multifilament yarns having the same number of single fibers per yarn and have the same fineness, of which fabric tissue is plain weaving, whose warps and woofs satisfy the above-described equation of $W=k\cdot(D/\rho)^{5/9}$, whose weaving densities in the directions of the warps and woofs are the same, whose weight is within the range of 120–250 g/m^2, and which has a cover factor K_c within the range of 90–99.8% are especially suited for the present invention. If the number of single fibers per one multifilament yarn is 3000, the fabric is even more preferred.

In general, woven fabrics, except for those having specific fabric tissues, are highly anistropic since the warps and woofs extend in the directions which are at right angles. However, if the numbers of fibers per a multifilament yarn in the warps and woofs, as well as the finenesses of the warps and woofs are identical, the characteristics in the directions at right angles are the same. Therefore, by laying-up the fabrics shifting a prescribed angle, e.g., 45°, pseudo-isotropic characteristics can easily be attained. Further, from the view point of manufacturing process, if the number of single fibers per yarn and the finenesses of the warps and woofs are identical, and if the weaving densities are identical in the warp and woof directions, the size of a mesh is identical in the warp and woof directions. Therefore, by opening the multifilament yarns to the same degree in both the directions, the width-enlarging and flattening of the yarns can easily be attained.

Further, if the fabric tissue is plain weaving, a thin and stable woven fabric in which the deformation of the meshes is small, may be obtained.

Further, if the number of single fibers per yarn and the finenesses of the warps and woofs are identical, if the weaving densities are identical in the warp and woof directions, and if the weight is 120–250 g/m^2, the cover factor K_c is not too small, the bending of the multifilament yarns at the intersections is smaller, so that the breakage by the concentration of stress can surely be avoided, and the irregularity in the surface is small, thus it is preferred. From the view point of manufacturing process, in the fabric having such a weight per a unit area, the restraint by the yarns each other is small in spite of the fact that the fabric tissue is plain weaving, and the size of the mesh is small, so that the opening, width-enlarging and flattening of the yarns can be easily attained with water jets. The weight of the fabric may more preferably be 140–195 g/m^2.

As the resin composition to be impregnated to such a woven fabric that satisfies the above-described equation of $W=k\cdot(D/\rho)^{5/9}$ and has a cover factor K_c of 90–99.8%, since resin compositions having relatively low viscosities are preferred to reduce the porosity, a resin composition containing an epoxy resin, a curing agent and a solid NBR which has a functional group and does not have a cross-linked structure is preferred.

It is more preferred that the resin composition just mentioned above have a complex coefficient of viscosity $\eta_{0.5}$ determined at 80° C. under a vibration frequency of 0.5 Hz during heating from 50° C. at a rate of 1.5° C./min of 100–1500 poise, and has a minimum complex coefficient of viscosity η_{min} determined at 80° C. under a vibration frequency of 0.5 Hz during heating from 50° C. at a rate of 1.5° C./min of 50–300 poise.

For the purpose of controlling the viscosity of the resin, or improving physical properties of the composite, such as compression strength and toughness, the cloth prepreg of the present invention may contain particles of calcium carbonate, talc, mica, silica, carbon black, silicon carbide, alumina hydrate or the like. Although the content of such particles is not restricted as long as they adversely affect the advantageous effects of the present invention, the content of the particles may usually be 0.1 to 3.0% based on the weight of the epoxy resin composition.

The cover factor K_p of the cloth prepreg of the present invention is 97–99.9%. It should be noted that the cover factor K_p is not the above-described cover factor K_c of the woven fabric, but is the cover factor of the cloth prepreg after the resin composition is impregnated into the woven fabric.

If the cover factor K_p is less than 97%, the degree of crushing of the meshes which are clearances formed among the warps and woofs of the reinforcing woven fabric is insufficient, so that pores are likely to be formed in the honeycomb fabricated plate, and the burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials, is not promoted. On the other hand, if the cover factor K_p is more than 99.9%, the drapability which is an important characteristic of a prepreg, is largely decreased.

In contrast, if the cover factor K_p is within the range of 97–99.9%, the porosity of the honeycomb fabricated panel is largely decreased while keeping the good drapability intrinsic to the cloth prepreg.

Further, in the cured plate obtained by curing the above-described cloth prepreg, the reinforcing fibers are uniformly distributed and the cover factor is large, so that cured plate excels in the burn-through property, that is, a property to prevent the penetration of flame during fire, that is important for interior materials.

The cover factor K_p is determined by the same method as the above-described method for determining the cover factor K_c, except that cloth prepreg is subjected to the measurement in place of the woven fabric.

The prepreg of the present invention may be prepared, in principle, by a conventional method for pro-

ducing prepregs employing an epoxy resin as a matrix resin. Although the prepreg may be prepared by impregnating the reinforcing woven fabric with the resin composition after the resin composition is dissolved in an appropriate solvent (i.e., wet process), if the above-described epoxy resin composition is used, a prepreg having no porosity can be prepared by the non-solvent method (hot-melt method) by which pores are otherwise likely to be formed. Since the above-described epoxy resin has high viscosity and yet has thixotropic property, the resin coating by the hot-melt method is unexpectedly easy.

The solid rubber having the weakly cross-linked structure forms micro-phases dispersed in the epoxy resin so as to give high viscosity and high thixotropic property to the resin. If the prepreg employing this resin as a matrix resin is used as a surface material of the honeycomb fabricated panel, the formation of pores which likely to be formed in the interlayer zones is drastically reduced. Since the epoxy resin composition containing the solid rubber has high viscosity and yet has thixotropic property, the resin coating by the hot-melt method is unexpectedly easy.

Further, the addition of the solid rubber having the weakly cross-linked structure promotes the flexibility and adhesiveness of the resin, so that appropriate tackiness and drapability are given, while not deteriorating the high elastic modulus, high thermal resistance and high solvent resistance which are intrinsic to a thermosetting resin.

When a resin film is prepared by the hot-melt method, if the viscosity of the resin is high, film-formation is usually difficult. However, since the solid rubber having a weakly cross-linked structure gives high thixotropy even if the viscosity is high, the resin coating by the hot-melt method is unexpectedly easy.

In cases where the solid rubber having a weakly cross-linked structure is used, when a prepreg is produced by the hot-melt method, the impregnation of the resin may preferably be carried out in two steps wherein the impregnation pressure in the first step is higher than in the second step. In this case, the resin composition which is impregnated in the first impregnation step may preferably have a complex coefficient of viscosity $\eta_{0.02}$ measured at 80° C. under a vibration frequency of 0.02 Hz of not less than 5000 poise and less than 40,000 poise, and the resin composition which is impregnated in the second impregnation step may preferably have a complex coefficient of viscosity $\eta_{0.02}$ measured at 80° C. under a vibration frequency of 0.02 Hz of 40,000–400,000 poise. Further, it is preferred to impregnate a resin composition containing an epoxy resin, at least one curing agent selected from the group consisting of aromatic amine curing agents, acid anhydride curing agents, dicyandiamide curing agents and novolak curing agents, and a solid rubber, in the first impregnation step and to impregnate a resin composition further containing polyether sulfone in addition to the components just mentioned above in the second impregnation step.

In the thus obtained prepreg, the resin composition impregnated in the first impregnation step constitutes an inner layer and the resin composition impregnated in the second impregnation step constitutes a surface layer. This structure is preferred since the porosity in the cured plate can be made small.

By dividing the impregnation process into two steps, the resin content of the prepreg after the first step may be made small so that the pressing out of the resin can be prevented even if a high impregnation pressure is applied. As a result, the quality of the finally obtained prepreg can be made high and the porosity of the fabricated plate can be extremely reduced.

In view of effectively preventing the pressing out of the resin even when a high impregnation pressure is applied and providing a prepreg having good impregnation property so as to provide a final prepreg having high quality, the resin content W_R of the intermediate prepreg after the first impregnation step may preferably be 25–30%, more preferably 27–29%. The resin content of the final prepreg may usually be 30 to 50%, although not restricted, irrespective whether the prepreg is prepared by the two-step process or one-step process.

The impregnation linear pressure (maximum contact stress) applied during the first impregnation step may preferably be not less than 1000 kg/cm^2, more preferably not less than 1200 kg/cm^2.

The impregnation linear pressure (maximum contact stress) σ_H (kg/cm^2) is calculated from the following Hertz' elastic contact theory when two cylindrical rolls made of the same material are used:

$$\sigma_H(\mathrm{kg/cm^2})=0.418(PE/Lr^*)^{\frac{1}{2}}$$

(wherein P represents the load applied to the rolls, E represents the elastic modulus of the rolls, L means the contact length of the rolls, r* represents radius of curvature represented from radii r_1 and r_2 of the two rolls which is calculated from the following equation:

$$(1/r_1)+(1/r_2)=1/r^*)$$

By preparing an intermediate prepreg having a good impregnation property in the first impregnation step, even if the second impregnation step is carried out at an impregnation pressure which is low enough to prevent the pressing out of the resin, a final prepreg having good impregnation property can be obtained. The thus obtained prepreg has a high stability of the resin content W_R, and its tackiness is also good.

In view of preventing the reduction in strength due to voids and preventing the degradation of the physical properties of the composite due to the repeated freezing of water, the ratio B of the area occupied by the voids in an optional cross-section may preferably be not more than 0.5%.

The impregnation property can be evaluated by curing the prepreg under the conditions in which the matrix resin does not substantially flow during the curing reaction, observing a polished cross-section of the cured prepreg and determining the percentage of the area of the non-impregnated region.

To clearly distinguish non-impregnated region from impregnated region when a cross-section of the prepreg is observed, it is necessary to polish the cross-section. To this end, it is necessary to heat the prepreg to cure. However, if a thermosetting matrix resin is heated, the viscosity is once decreased with the raise of the temperature and flowing of the resin is observed. If the resin flows during the curing process, the resin flows into the regions which are not impregnated in the original prepreg, so that the impregnation property thus determined does not reflect the state of the original prepreg. Therefore, in the curing of the prepreg, the increase in the viscosity due to the reaction of the resin must be more than the decrease in the viscosity due to the raise

of the temperature. This may be attained by gradually raising the temperature to cure the resin. For example, in cases where a resin mixture containing a mixture of glycidylamine type epoxy resin and bisphenol A type epoxy resin, and an equivalent amount of diaminodiphenylsulfone as a curing agent is used, the preferred rate of raising temperature is not more than 1° C./hour.

When a polished cross-section of the thus cured prepreg is observed with an optical microscope, the non-impregnated regions in the prepreg is observed as voids in which the matrix resin does not exist. The void content B is calculated by the following equation:

$$B=(b/a)\times 100\ (\%)$$

(wherein "a" represents the area of an optional region in a photomicrograph of a cross-section and "b" represents the area occupied by voids).

The relationship between the void content B and the porosity P in the composite will now be described.

The methods for fabricating the composite using a prepreg include vacuum bag method, autoclave method using a vacuum bag and press method. Among these, to fabricate a composite with high performance, autoclave method using a vacuum bag is preferably employed.

Thus, a composite was prepared by the autoclave method using a vacuum bag, employing a prepreg whose void content B is known, and the optional region in an optional polished cross-section was observed with a microscope. As a result, a positive correlation was observed between the void content B and the porosity P in the composite. That is, if the void content B is small, the porosity P in the composite is small. Further, it was found that if the void content B is not more than 0.5%, by employing a prepreg which is appropriately flow-controlled, a composite having a porosity of substantially 0 can be obtained. Although the upper limit of the void content B of the more preferred range is 0.3%, it is not necessary to lower the void content B below the lower limit of 0.05%. If the void content B is unnecessarily low, in the wet method, a drying step at a high temperature for a long time is necessary to evaporate the solvent more, and in the hot-melt method, a higher temperature is necessary to decrease the viscosity of the resin, so that in both cases, the reaction of the resin is accelerated. As a result, the tackiness and drapability of the prepreg may be deteriorated.

According to a second aspect of the present invention, a prepreg comprising the above-described reinforcing fabric according to the present invention and a thermoplastic matrix resin is provided. Examples of the thermosetting matrix resin include epoxy resins, unsaturated polyester resins, phenol resins, polyimide resins, and bismaleimide resins at B stages. Such a prepreg may be prepared according to a conventional method in which the reinforcing fabric is impregnated with the above-mentioned thermosetting resin. The content of the thermosetting resin in the prepreg may preferably be 30–50% by weight, more preferably 35–45% by weight.

The present invention will now be described by way of examples thereof. It should be noted that the examples are presented for the illustration purpose only and should not be interpreted in any restrictive way.

EXAMPLE 1

An epoxy resin composition having the following composition was prepared in a kneader. The resin composition was heated at 80° C. for a short time and coated on a releasing paper to obtain a resin film. In the following Examples and Comparative Examples, all parts are by weight unless otherwise specified.

<Epoxy Resin>	
Brominated bisphenol A type Solid Epoxy (EPC152)	13.4 parts
Bisphenol A type Liquid Epoxy (EP 828)	26.8 parts
Tetraglycidyldiaminodiphenyl methane (ELM 434)	17.0 parts
Bisphenol F type Liquid Epoxy (EPC830)	8.5 parts
<Curing Agent>	
4,4'-DDS (4,4'-diaminodiphenylsulfone)	23.0 parts
BF_3.MEA (BF_3 monoethylamine complex)	0.3 parts
<Solid Rubber>	
Carboxyl-terminated solid NBR having weakly cross-linked structure	8.0 parts
<Thermoplastic Resin>	
Hydroxyl-terminated polyether sulfone (PES100P)	3.0 parts
Total	100.0 parts

This resin film was set in a prepreg machine and impregnated into a plain-woven fabric made of carbon fibers (TORAYCA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric, to obtain a prepreg having a resin content W_R of 40%. This prepreg had an excellent tackiness and drapability, and its cover factor K_p was 99%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken, which is shown in FIG. 3. In the entire cross-section, pores are not substantially observed and the porosity P was 0.05%.

Twenty of the thus prepared prepregs were laid-up in the same direction and the resulting laminate was cured. The toughness C_{IC} of the obtained cured plate was measured by the double cantilever method, which was 9.5 pounds/inch.

Two prepregs were laid-up and the laminate was cured. The resulting cured plate was tested for its burn-through characteristics. The cured plate was placed on a tripod and heated with a gas burner under the cured plate. The time required for the flame to penetrate the plate was measured, which was 280 seconds.

Comparative Example 1

An epoxy resin composition having the following composition was prepared in a kneader. The resin composition was heated at 80° C. for a short time and coated on a releasing paper to obtain a resin film.

<Epoxy Resin>	
Brominated bisphenol A type Solid Epoxy (EPC152)	13.4 parts
Bisphenol A type Liquid Epoxy (YD 128)	26.8 parts
Tetraglycidyldiaminodiphenyl methane (ELM 434)	17.0 parts
Bisphenol F type Liquid Epoxy (EPC830)	8.5 parts
<Curing Agent>	
4,4'-DDS (4,4'-diaminodiphenylsulfone)	23.0 parts
BF_3.MEA (BF_3 monoethylamine complex)	0.3 parts
<Liquid Rubber>	
Epoxy-terminated liquid NBR (TSR-601)	8.0 parts
<Thermoplastic Resin>	
Hydroxyl-terminated polyether sulfone (PES100P)	3.0 parts

-continued

Total	100.0 parts

This resin film was set in a prepreg machine and impregnated into a plain-woven fabric made of carbon fibers (TORAYCA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric, to obtain a prepreg having a resin content W_R of 40%. The cover factor K_p of this prepreg was 92%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken, which is shown in FIG. 4. Pores are observed in the substantial area of the interlayer zones and the porosity P was 3.0%.

Twenty of the thus prepared prepregs were laid-up in the same direction and the resulting laminate was cured. The toughness C_{IC} of the obtained cured plate was measured by the double cantilever method, which was 3.5 pounds/inch.

Two of the prepreg were laid-up and the laminate was cured. The resulting cured plate was tested for its burn-through characteristics. The cured plate was placed on a tripod and heated with a gas burner under the cured plate. The time required for the flame to penetrate the plate was measured, which was 130 seconds.

EXAMPLE 2

An epoxy resin composition having the following composition was prepared in a kneader. The resin composition was heated at 80° C. for a short time and coated on a releasing paper to obtain a resin film. The weight of the resin paper was 40 g/m².

<Epoxy Resin>	
Brominated bisphenol A type Solid Epoxy (EPC152)	13.7 parts
Bisphenol A type Liquid Epoxy (YD 128)	20.3 parts
Tetraglycidyldiaminodiphenyl methane (ELM 434)	17.3 parts
Bisphenol F type Liquid Epoxy (EPC830)	16.7 parts
<Curing Agent>	
4,4'-DDS (4,4'-diaminodiphenylsulfone)	23.5 parts
BF_3.MEA (BF_3 monoethylamine complex)	0.5 parts
<Liquid Rubber>	
Epoxy-terminated liquid NBR (TSR-601)	7.0 parts
<Thermoplastic Resin>	
Hydroxyl-terminated polyether sulfone (PES100P)	1.0 part
Total	100.0 parts

This resin film was set in a prepreg machine and the first impregnation step was carried out by impregnating the resin composition into a plain-woven fabric made of carbon fibers (TORAYCA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric. The impregnation temperature was 130° C. and the impregnation linear pressure was 1400 kg/cm². The resin content W_R of the intermediate prepreg obtained in this first impregnation step was 29%. In spite of the high impregnation pressure, the resin was not pressed out and an intermediate prepreg having the prescribed resin content was obtained.

A resin composition for the second impregnation step, which had the same composition as that for the first impregnation step was coated on a releasing paper to obtain a resin film having a weight of 25 g/m². The second impregnation step was carried out by impregnating the intermediate prepreg obtained in the first impregnation step with the resin composition from both sides of the prepreg under heat. The impregnation temperature was 100° C. and the impregnation linear pressure was 690 kg/cm². A prepreg having a resin content W_R of 40% was obtained. The thus obtained final prepreg had excellent impregnation property, tackiness and drapability. The cover factor K_p of the thus obtained final prepreg was 98%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken. Pores were not substantially observed in the interlayer zones and the porosity P was 0.04%.

Comparative Example 2

Using the epoxy resin composition used in Example 2, a prepreg was prepared by a single impregnation step.

That is, the epoxy resin composition was heated at 80° C. for a short time and was coated on a releasing paper to obtain a resin film having a weight of 65 g/m². This resin film was set in a prepreg machine and impregnation was carried out in a single step by impregnating the resin composition into a plain-woven fabric made of carbon fibers (TORAYCA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric. The impregnation temperature was 120° C. and the impregnation linear pressure was 1400 kg/cm². When the resin composition was pressed to the reinforcing fabric under a high pressure, the resin was pressed out, so that the obtained prepreg had a resin content W_R of only 34%. The cover factor K_p of this prepreg was 95%.

Comparative Example 3

A prepreg was prepared by the same process as in Comparative Example 2 except that the impregnation linear pressure was 900 kg/cm². When the resin composition was pressed to the reinforcing fabric, the resin was not pressed out and a prepreg having a resin content W_R of 40% was obtained. The cover factor K_p of this prepreg was 98%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken. Pores were observed in substantial parts of the interlayer zones and a number of pores were observed in the resin layer, which are considered to be formed due to the insufficient impregnation of the resin. The porosity P was 1.5%.

Comparative Example 4

Using the resin composition used in Example 2, a prepreg was prepared by a two-step impregnation process. The resin composition formulated in a kneader was heated at 80° C. for a short time and was coated on a releasing paper to obtain a resin film having a weight of 40 g/m². This resin film was set in a prepreg machine and a first impregnation step was carried out by impregnating the resin composition into a plain-woven fabric made of carbon fibers (TORAYCA C07373, commercially available from TORAY INDUSTRIES, INC.) from both sides of the fabric. The impregnation temperature was 130° C. and the impregnation linear pressure was 690 kg/cm². The resin content W_R of the thus obtained intermediate prepreg obtained by this first impregnation step was 29%.

The epoxy resin composition having the same composition as that used in the first impregnation step was coated on a releasing paper to obtain a resin film for the second impregnation step, having a weight of 25 g/m^2. The intermediate prepreg obtained by the first impregnation step was impregnated with the epoxy resin composition to carry out the second impregnation step. The impregnation linear pressure was 690 kg/cm^2 which was the same as that in the first impregnation step, and the impregnation temperature was 100° C. A final prepreg having a resin content W_R of 40% was obtained. The cover factor K_p of this prepreg was 98%.

A honeycomb panel was fabricated laying-up this prepreg and a photomicrograph of a polished cross-section thereof was taken. Pores were observed in substantial parts of the interlayer zones and a number of pores were observed in the resin layer, which are considered to be formed due to the insufficient impregnation of the resin. The porosity P was 2.5%.

Reference Example 1

Using "TORAYCA" T300 yarns (average number of twisting: 0.8 turns/m, average diameter of single fiber: 7 μm, average number of fibers per yarn: 3000, fineness: 1800 denier, specific gravity: 1.76) as warps and woofs, a woven fabric was prepared by plain weaving. The widths of each warp and woof were 1.47 mm and 1.49 mm, respectively, and the size of the meshes was 0.57 mm and 0.59 mm in the directions of warp and woof, respectively. The weaving densities in the warp and woof directions were both 4.85 yarns/cm (warp pitch: about 2.06 mm). The weight of the fabric was 194 g/m^2 and the thickness of the fabric was 0.31 mm.

The above-described woven fabric was made to run in the warp direction at a rate of 1.5 m/min and the opening, width-enlarging and flattening operation of the yarns was performed by using water jets. The diameter of the nozzle was 0.13 mm, the nozzle pitch was 0.6 mm and the beating force per one water jet was 0.6 gf.

In the thus treated woven fabric, the yarns were well opened and the widths of the warps and woofs were enlarged to 1.71 mm and 1.91 mm, respectively. The thickness was 0.28 mm, and the cover factor K_c was 99%. The obtained woven fabric was thin and the irregularities in the surface were very small. Further, cutting of single fibers and generation of down were not observed.

EXAMPLE 3

An epoxy resin composition having the following composition was prepared in a kneader.

<Epoxy Resin>	
Brominated bisphenol A type Solid Epoxy (EPC152)	63.0 parts
Bisphenol A type Liquid Epoxy (EPC828)	127.0 parts
Tetraglycidyldiaminodiphenyl methane (ELM 434)	40.0 parts
Bisphenol F type Liquid Epoxy (EPC830)	20.0 parts
<Curing Agent>	
4,4'-DDS (4,4'-diaminodiphenylsulfone)	80.0 parts
<Solid Rubber>	
Carboxyl-terminated solid NBR (NIPOL 1072)	25.0 parts (7.0 wt %)

During the process of heating this resin composition from 50° C. at a rate of 1.5° C./min, the complex coefficient of viscosity $\eta_{0.5}$ measured at 80° C. under a vibration frequency of 0.5 Hz was 700 poise and the minimum complex coefficient of viscosity η_{min} was 90 poise.

This resin composition was heated at 80° C. for a short time and was coated on a releasing paper to obtain a resin film.

This resin film was set in a prepreg machine and impregnation of the resin was performed from the both sides of the carbon fiber woven fabric prepared in Reference Example 1. The impregnation temperature was 100° C. and the impregnation pressure was 4 kgf/cm^2 to obtain a prepreg with a resin content of 40%, having excellent tackiness and drapability were obtained. The cover factor K_p of this prepreg was 99% . This prepreg was cured in a hot air oven by heating the prepreg to 180° C. at a rate of 0.5° C./hour. A photomicrograph of a polished cross-section of the cured prepreg was taken and the void content B was measured, which was 0.15%.

One prepreg thus obtained was placed on an aluminum plate to which a silicone-based releasing agent was applied. On the prepreg, another prepreg was placed such that the direction of warps of the reinforcing fabric of the prepreg was shifted by 45° from the direction of warps of the reinforcing fabric of the first placed prepreg. On the second prepreg, a honeycomb core made of aramide paper impregnated with a thermally resistant phenol resin, having a size of the inner space of the cells of ⅛ inch (about 3.2 mm) and having a thickness of ½ inch (about 12.7 mm) was placed. On the honeycomb core, the above-described two prepregs were laminated in the direction such that their reinforcing fabrics constitute the mirror image of the reinforcing fabrics of the above-mentioned first two prepregs under the honeycomb core. The entire structure was packed in a fluorine-contained resin film.

The resulting packed structure was placed in an autoclave and was heated to 180° C. at a rate of 1.5° C./min under a pressure of 3 kgf/cm^2 while reducing the pressure in the pack. The structure was left to stand at this temperature for two hours to cure the epoxy resin of the cloth prepreg to form skins and to adhere the skins with the honeycomb core.

A cross-section of the thus obtained honeycomb sandwich panel was observed with a microscope, which is shown in FIG. 5. The porosity P was 0.01%.

Comparative Example 5

The same procedure as in Example 3 was repeated except that carbon fiber woven fabric "C07373Z" of which yarns are not opened was used as the reinforcing fabric. The cover factor K_p was 96%. The porosity P of the obtained composite was 0.3%, which is inferior to that attained in Example 3.

Comparative Example 6

The same procedure as in Example 3 was repeated except that 12% by weight of a solid NBR "NIPOL 1072" was used. The cover factor K_p of the obtained prepreg was 99% . Although the minimum complex coefficient of viscosity η_{min} was raised to 500 poise, the complex coefficient of viscosity $\eta_{0.5}$ at 80° C. was 2500 poise, so that the void content B was as much as 0.8%. As a result, the porosity P of the obtained composite was 0.5%, which was inferior to that attained in Example 3.

Comparative Example 7

The same procedure as in Example 3 was repeated except that 3% by weight of a solid NBR "NIPOL 1072" was used. The cover factor K_p of the obtained prepreg was 99% . Since the complex coefficient of viscosity $\eta_{0.5}$ at 80° C. was as low as 350 poise, the void content B was as much as 0.8%. The minimum complex coefficient of viscosity was as low as 15 poise, so that the porosity P of the composite was 0.4%, which was inferior to that attained in Example 3. A photomicrograph of a cross-section of the honeycomb sandwich panel is shown in FIG. 4.

The results of Example 3 and Comparative Examples 5–7 are shown in Table 1.

Example 4 Preparation of Reinforcing Fabric

To a twisted yarn made of carbon fibers, 0.8% by weight of an epoxy-based sizing agent was applied and the resultant was dried. The yarn was then untwisted to 0.8 turns/m. The average diameter of the carbon fibers was 7 μm, the number of fibers per yarn was 3,000, the fineness of the yarn was 1,800 denier and the specific gravity of the yarn was 1.76. This yarn is commercially available from TORAY INDUSTRIES, INC., under the trademark of TORAYCA T300. Using TORAYCA T300 as warps and woofs, a plain-woven fabric was prepared. The widths of the warps and woofs were 1.47 mm and 1.49 mm, respectively. The sizes of the mesh in the warp and woof directions were 0.57 mm and 0.59 mm, respectively. The weaving densities in both the warp and woof directions were 4.85 yarns/cm (warp pitch: about 2.06 mm). The weight of the fabric was 194 g/m^2 and the thickness was 0.31 mm.

The thus obtained fabric was subjected to the opening, width-enlarging and flattening operation while moving the fabric in the warp direction at a rate of 1.5 m/min as shown in FIG. 1. A nozzle apparatus having nozzle holes with a diameter of 0.13 mm and with a nozzle pitch of 0.6 mm was used. The punching force per one water jet was 0.6 gf.

In the resulting fabric, the fibers were well opened and the warps and woofs were enlarged and flattened to widths of 1.71 mm and 1.91 mm, respectively. The thickness of the fabric was 0.28 mm and the cover factor was about 99% . Thus, the fabric was thin and the irregularities in the surface were very small. Further, breakage of fibers and generation of nap were not observed.

Comparative Example 8

The same procedure as in Example 4 was repeated except that the punching force per one Jet water was 4.5 gf. In the obtained fabric, frequent breakage of the fibers was observed and the fabric looked like a nonwoven fabric made of short fibers.

EXAMPLE 5

Using the yarn made of carbon fibers used in Example 1, a plain-woven fabric was prepared. The widths of the warps and woofs were 1.60 mm and 1.49 mm, respectively. The sizes of the mesh in the warp and woof directions were 1.37 mm and 1.26 mm, respectively. The weaving densities in both the warp and woof directions were 3.5 yarns/cm (warp pitch: about 2.86 mm). The weight of the fabric was 140 g/m^2 and the thickness was 0.29 mm.

The thus obtained fabric was subjected to opening, width-enlarging and flattening operation as in Example 1. In the resulting fabric, the warps and woofs were enlarged and flattened to widths of 2.17 mm and 2.09 mm, respectively. The thickness of the fabric was 0.23 mm and the cover factor was about 96%. Thus, the fabric was thin and the irregularities in the surface were very small. Further, breakage of fibers and generation of nap were not observed.

EXAMPLE 6

The fabric prepared in Example 5 was impregnated with a phenol resin at B stage to obtain a prepreg. The content of the phenol resin in the prepreg was 44% by weight.

Six plies of the thus obtained prepreg were stacked aligning the directions of the warps and the laminate was heated at 170° C. for one hour at a pressure of 7 kg/cm^2 to obtain a CFRP plate with a thickness of 1.03 mm. The content by volume of the carbon fibers in the thus obtained CFRP plate was 46.5%.

Observation of the obtained CFRP plate revealed that the carbon fibers were well dispersed and no portions containing excess resin and no voids existed.

A test strip having a width of 25 mm and a length of 230 mm was cut out from the obtained CFRP plate and the test strip was subjected to the tensile strength tests according to JIS K7073. The test results are as follows:

Tensile Strength: 48.5 kg/mm^2
Tensile Elongation: 5480 kg/mm^2
Tensile Breaking Strain: 0.94%
Tensile Proportional Limit Strain: 0.94%

Comparative Example 9

A prepreg was prepared in the same manner as in Example 6 except that the fabric described in Example 5 before the opening, width-enlarging and flattening operation was used, and a CFRP was prepared therefrom also in the same manner as in Example 6. The thus obtained CFRP plate had a thickness of 1.06 mm and a content by volume of carbon fibers of 45.1%.

Large portions having excess resin were observed at the meshes and large voids which can be observed even with naked eyes were observed in the vicinities thereof.

The thus obtained CFRP plate was subjected to the same tensile tests as in Example 6. The test results are as follows:

Tensile Strength: 47.5 kg/mm^2
Tensile Elongation: 5460 kg/mm^2
Tensile Breaking Strain: 0.95%
Tensile Proportional Limit Strain: 0.60%

When compared with the prepreg prepared in Example 6, this prepreg was thicker and the content by volume of the carbon fibers was smaller than that of the prepreg of Example 6 in spite of the fact that the content of the phenol resin in the prepreg was the same. Although the tensile strength, tensile elongation and tensile breaking strain were not very different from those of the prepreg of Example 6, the tensile proportional limit strain was 0.60%. This means that the linearity between stress and strain is lost before the final rupture. In contrast, with the prepreg prepared in Example 6, the tensile proportional limit strain was 0.94%, which means that the linearity between stress and strain is kept up to the final rupture.

TABLE 1

	Example 3	Comparative Example 5	Comparative Example 6	Comparative Example 7
Type of Carbon Fiber Fabric	Opened	Non-opened	Opened	Opened
Amount of "NIPOL 1072" Added(%)	7	7	12	3
Viscosity at 80° C. (poise)	700	700	2500	350
Minimum Viscosity (poise)	90	90	500	15
Void Content B(%) in Prepreg	0.15	0.6	0.8	0.1
Porosity P(%) of Composite	0.01	0.3	0.5	0.4

We claim:

1. A reinforcing fabric comprising warps and woofs which are multifilament yarns made of carbon fibers, the widths W, and finenesses D, of said warps and woofs satisfying the equation:

$$W=k\cdot(D/\rho)^{5/9}$$

wherein k represents 3.5×10^{-2} - 10.0×10^{-2} and ρ represents specific gravity of said carbon fibers, said woven fabric having a cover factor K_c of 90.0–99.8%, and wherein said warps and woofs are twisted to not more than 5 turns/m and each of said warps comprises not less than 3000 fibers.

2. The fabric of claim 1, wherein said fabric is a plain-woven fabric in which the finenesses of said warps and woofs are the same, each of said warps and woofs comrprises 3000 fibers.

3. The fabric of claim 2, which has a weight per an unit area of 120–250 g/m^2.

4. A reinforcing fabric comprising warps and woofs which are multifilament yarns made of carbon fibers, the widths W, and finenesses D, d:denier, of said warps and woofs satisfying the equation:

$$W=k\cdot(D/\rho)^{5/9}$$

wherein k represents 4.5×10^{-2} - 10.0×10^{-2} mm·d$^{-5/9}$ and ρ represents specific gravity of said carbon fibers, said woven fabric having a cover factor K_c of 90.0–99.8%, and wherein said warps and woofs are twisted to not more than 5 turns/m and each of said warps comprises fewer than 3000 fibers.

* * * * *

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(54) INTUMESCENT COMPOSITION AND METHOD

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(58) **Field of Search** 524/124, 429; 428/704; 252/609

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(57) **ABSTRACT**

An aqueous composition containing a hardenable binder of a melamine compound, such as an acid-hardenable melamine-formaldehyde resin, and an acidic phosphorus compound, such as a nitrogen-containing phosphorus compound made from either phosphoric acid or phosphorus acid, and expandable graphite flake, which composition is curable to an intumescent composition.

18 Claims, No Drawings

INTUMESCENT COMPOSITION AND METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention broadly relates to a composition useful for imparting fire resistance to a variety of substrates, particularly for materials used in the building and construction industry. More particularly, this invention provides an aqueous composition containing as essential components a binder of a melamine compound and an acidic phosphorus compound, and expandable graphite flakes. After hardening the aqueous composition, it acts as an intumescent and imparts fire resistance to substrates treated with the composition.

2. Description of Related Art

Intumescent coatings are commonly applied to the surface of construction materials. Such coatings serve, for example, to prevent the spread of fire. Intumescent coatings are also applied to the surface of other flammable substrates, to reduce their flammability. U.S. Pat. No. 4,198,328 for example, describes an intumescent paint which includes a source of phosphoric acid, a carbon source and an expanding agent. These components are bound together by a conventional polymeric binder. Binders have included acrylic styrene or vinyl toluene copolymer, a styrene or vinyl toluene-butadiene-copolymer, a styrene or vinyl toluene-acrylonitrile-copolymer, polyurethane resins, alkyl resins and the like. Alternatively, polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, urea or melamine-formaldehyde resins and vinyl chloride-vinylidene chloride copolymers have been used. The use of epoxy resins in combination with various amino-functional curing agents also is known. In all of these formulations chlorinated paraffins or optionally chlorinated phosphate esters may be employed as plasticizers.

Other intumescent systems are also known. GB-A-2,151,237 discloses water-insoluble formulations which contain chlorinated polymers, novolak resin and chlorinated or phosphorylated plasticizers. GB-A-2,012,296 describes a three-layer intumescent paint which uses as the intermediate layer formulations which contain expandable graphite, hydrated alumina and binder systems based on halogenated elastomers and alkyl phenol-formaldehyde resins. The binder, in concert with a silicate top coating, functions to prevent the expanded graphite from crumbling and cracking. GB-A-1,604,908 mentions products with vermiculite and inorganic fibers as filler as well as elastomeric binders and clay.

Intumescent, fire resistant compositions act by forming an expanded, insulating layer of a hardly flammable material under the action of heat. The expanded layer shields the substrate from oxygen and/or from overheating and thereby prevents or delays the spread of flame, and prevents or at least delays reductions in the mechanical and static properties of structural supporting elements caused by heat.

A greater expansion (intumescence) produces thicker protective layers, but at the same time the thicker layers, generally due to their reduced mechanical stability, often are more easily detached from the substrate thus becoming less effective.

Conventional intumescent systems consist of a binder of the above type including urea-formaldehyde resins and melamine-formaldehyde resins, a char or carbon skeleton forming substance (typically referred to as "carbonific"), an

expanding agent (typically referred to as "spumific") and an acid forming substance as essential components. As carbonifics, organic polyhydroxy compounds such as pentaerythritol, dipentaerythritol, tripentaerythritol, starch and sugars have been employed. Examples of spumifics are nitrogen-containing compounds such as melamine, melamine salts, melamine derivatives, urea, dicyandiamide and guanidine. The spumific effects the formation of a foamed (intumescent) layer by emission of an inert gas. As acid forming substances usually an aminophosphate, mainly ammonium phosphates and amine phosphates, preferably ammonium polyphosphate, and melamine phosphate, have found use. Examples of further additives are inorganic fibers which are to increase the mechanical strength of the intumescent layer and/or to prevent the dripping thereof, and metal oxides which act as smoke suppressants. Typical examples of such compositions can be found in U.S. Pat. Nos. 4,442,157, 4,638,538, 3,562,197, and GB-A-755,551.

Upon exposure to a flame, an intumescent composition swells up with the formation of a foam which repels the action of the fire. Many intumescence compositions, used, for example, as fire-preventive coatings or fire-preventive cements, on exposure to a flame form carbonization foams, because they contain, as intumescence media, carbohydrates or phenolic, polyurethane or melamine resins in combination with a phosphoric acid donor. Inorganic materials, for example alkali metal silicates containing water, can also foam up on exposure to a flame, and also are employed for the purposes of fire prevention. However, since these silicates are sensitive to air, moisture and/or CO_2, they can only be used to a limited extent as intumescence media.

In most organic-compound based intumescence compositions, carbonisable compounds in combination with phosphorus compounds act as the intumescence media. The carbonization foams formed on exposure to a flame have, however, only a low mechanical strength, put up only a low resistance to flame erosion and are degradable by oxidation. Organic fire-preventive materials of this type can also contain aluminum hydroxide, the function of which is to assist the foaming up of the carbonization melt by splitting off water under the influence of heat, and to carry off heat.

The carbonization of organic melts is promoted by phosphorus compounds which liberate phosphoric acid. As noted above, ammonium phosphates are therefore frequently employed as phosphoric acid donors, but their good solubility in water has often been considered a disadvantage.

There is, therefore, still a need for intumescence compositions which are not degradable by oxidation, which are insensitive towards air, moisture and CO_2, which upon exposure to a flame become effective even at temperatures below 200° C., and which form as far as possible an intumescent foam having mechanical stability.

Accordingly it is an object of the present invention to provide a composition having integrated intumescent properties which avoids or at least alleviates disadvantages of conventional prior art intumescent systems described above.

Compliance with various fire resistance testing methods is an important consideration in developing fire resistant compositions because many regulatory agencies and building codes rely on these tests in determining the acceptance of building materials used in various applications. Insurance rates may also be affected by compliance with fire resistance testing methods. In the present invention, fire resistance of the composition was determined in part using the Cone Calorimetric Test (ASTM E1354), the Tunnel Test (ASTM E-84), the Heat Release Test (ASTM E-906) and the Smoke Test (ASTM E-662).

BRIEF DESCRIPTION OF THE INVENTION

In a first aspect, the present invention is directed to an intumescent composition comprising the hardened product of an aqueous composition containing as essential components a binder of a melamine compound and an acidic phosphorus compound, and expandable graphite flakes.

The invention also relates to an aqueous composition suitable for imparting fire resistance to a substrate, such as by coating or impregnating the substrate with a nascent intumescent composition, said aqueous composition comprising as essential components a binder of a melamine compound and an acidic phosphorous compound, and expandable graphite flakes.

In accordance with yet another aspect of the invention, a substrate is rendered fire resistant by treating said substrate with an aqueous composition comprising as essential components a binder of a melamine compound and an acidic phosphorus compound, and expandable graphite flakes. The resultant fire resistant article, comprises the substrate coated or impregnated with the hardened composition containing a binder of a melamine compound and an acidic phosphorus compound, and expandable graphite flakes.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, an intumescent composition is prepared by hardening an aqueous composition containing a binder of a melamine compound and an acidic phosphorus compound, and expandable graphite flakes. The binder constitutes a char-forming, phosphorus-containing intumescent which serves to hold the expanded graphite flakes in contact with a substrate under conditions of thermal stress such that the intumescent coating is maintained as a barrier against the spread of fire.

The present invention is based on this interaction between the expanding graphite flakes, which form "worm like" structures on exposure to heat, and the intumescent char formed from the intumescent binder of the acidic phosphorus compound and the melamine compound. The intumescent char formed from the binder, binds the expanded graphite to the substrate so as to create a composite structure having the mechanical and insulative performance critical to the success of a fire retardant system.

The melamine compound of the binder component of the composition can comprise melamine per se, a modified melamine or a melamine-formaldehyde resin. Suitable modified melamines include methylated melamines.

Melamine-formaldehyde (MF) resins can be used as the melamine compound and are generally preferred. MF resins suitable for preparing the intumescent composition of the present invention are well known to those skilled in the art. Such resins can be prepared using known techniques by reacting melamine and formaldehyde in an aqueous reaction medium at a melamine to formaldehyde mole ratio in the range of 1:1 to 1:6. Preferably, the melamine:formaldehyde mole ratio is in the range of 1:2 to 1:4. In the broad practice of the present invention, standard reaction conditions, procedures and reactants widely used for preparing aqueous melamine-formaldehyde resins that can be cured to an infusible state with an acid catalyst, can be used.

An MF resin is generally prepared by adding melamine to an aqueous formaldehyde solution. Normally, the reaction is conducted, at least initially, at an alkaline pH, a pH normally of 7 to 10 typically being satisfactory, and at a temperature in the range of 50°–100° C., more usually at 60°–90° C. A variety of techniques are known in the art for reacting melamine and formaldehyde in the presence of an alkaline catalyst. Oftentimes, the resin is reacted in stages with separate partial additions of either one or both of the reactants and the alkaline catalyst. In the broad practice of the present invention, however, any process for producing an acid-curable MF resin can be advantageously employed.

Formaldehyde useful for preparing the resin generally is supplied as an aqueous solution known in the art as "formalin". Formalin is an aqueous solution that typically contains from about 37% to about 50% by weight formaldehyde. Other forms of formaldehyde such as paraformaldehyde also can be used. Other aldehydes, which may be used in combination with formaldehyde to introduce specific properties into the MF resin, include aliphatic aldehydes such as acetaldehyde and propionaldehyde; aromatic aldehydes such as benzylaldehyde and furfural and other aldehydes such as aldol, glyoxal and crotonaldehyde, also can be used. Similarly, a portion of the melamine for the melamine compound component could be replaced by other aminotriazines such as dicyandiamine and benzoguanamine.

Suitable melamine-formaldehyde resins also include methylated melamine resins and resins which have been modified with aromatic glycidyl ethers and/or cycloaliphatic epoxides. Specific examples of modifiers of said type are 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexanecarboxylate and bisphenol-A-diglycidylether. These modifications may increase the strength of the cured composition and in the event of fire may result in an increased adhesion of the intumescent layer to the protected substrate. Preferably, the modifiers mentioned above are used in an amount such that they account for no more than about 1 to 15% by weight of the MF resin.

Sodium hydroxide generally is the alkaline catalyst of choice for synthesizing such melamine-formaldehyde resins. A non-limiting list of other potential alkaline catalysts includes, inter alia, other alkali metal hydroxides such as potassium hydroxide, alkali metal carbonates such as sodium and potassium carbonates, and alkaline earth metal oxides and hydroxides such as barium hydroxide, calcium hydroxide and calcium oxide. Organic amines also can be used in the broad practice of the invention.

Acid-curable melamine-formaldehyde resins useful in practicing the present invention, including water soluble MF resin powders, normally made by neutralizing and then spray-drying an aqueous MF resin solution, are items of commerce. Suitable commercial aqueous MF resin solutions and powdered MF resins for practicing the present invention are available, for example, from Cytec, BTL and Hoechst Celanese companies.

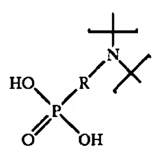
In the broad practice of the present invention, it also is possible to blend other acid-curable resins with the acid-curable melamine-formaldehyde resin component to provide certain property modifications to the base MF resin. For example, minor amounts of phenol-formaldehyde resins and urea-formaldehyde resins can be included in the aqueous compositions as modifiers. Normally, the total amount of such resin additives will be 50% or less, normally 30% or less, and most often 20% or less of the solids content of the aqueous composition.

The other essential constituent of the binder component of the composition of the present invention is the acidic phosphorus compound. Suitable acidic phosphorus compounds include the known phosphoric acid esters of polyhydroxy compounds (partial phosphate esters), as described in U.S. Pat. No. 5,387,655 (the disclosure of which is incorporated

by reference), and certain nitrogen-containing, acidic phosphorus compounds.

The phosphoric acid esters can be prepared by reacting a polyol or a mixture of polyols, such as pentaerythritol, glycerol, trimethylol propane and the like, with a polyphosphoric acid. The reaction is conducted to a constant acid value, upon the controlled addition of the phosphoric acid to the polyol(s) under a reduced pressure, with vigorous agitation and with control of the temperature (e.g., 100° to 150° C.).

Suitable nitrogen-containing acidic phosphorus compounds contain one or more moieties of the following formula:

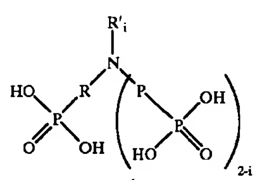


where R is selected from a C_1 to C_6 alkylene radical, a C_3 to C_7 cycloalkylene radical, an arylene radical and a divalent radical of the formula:

$$—(CH_2)_x—O—[(CH_2)_z—O]_y—$$

where x and z are integers of 1 to 6, and y is an integer from 0 to 2 and wherein the divalent radical is bonded to the phosphorus atom of said moieties through the terminal oxygen atom.

One preferred class of such nitrogen-containing acidic phosphorus compounds includes compounds of the following formula:

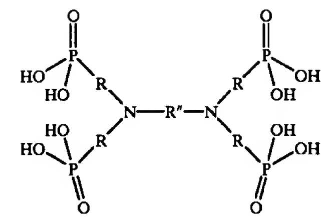


where R is selected from a C_1 to C_6 alkylene radical, a C_3 to C_7 cycloalkylene radical, an arylene radical and a divalent radical of the formula:

$$—(CH_2)_x—O—[(CH_2)_z—O]_y—$$

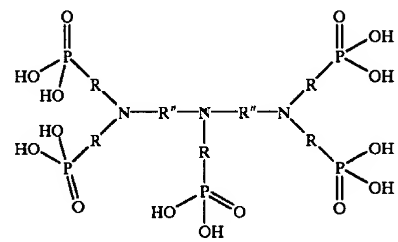
where x and z are integers of 1 to 6, and y is an integer from 0 to 2 and wherein the divalent radical is bonded to the phosphorus atoms of said compound through the terminal oxygen atom of said radical and where i is 0 or 1, and R' is selected from hydrogen, a C_1 to C_6 alkyl, a C_1 to C_6 alkoxy, a cycloalkyl and an aryl.

Another class of nitrogen-containing, acidic phosphorus compounds includes compounds of the formula:



where R" is a divalent organic radical, such as an alkylene group having from 1 to 12 carbon atoms and R has the same meaning noted above.

Yet another class of nitrogen-containing, acidic phosphorus compounds has the formula:



where R and R" have the same meanings as above.

One class of such compounds can be prepared by reacting (partially neutralizing) orthophosphoric acid (H_3PO_4) with an alkanol amine, and particularly a di- or tri-alkanol amine. Suitable alkanol amines may have the formula:

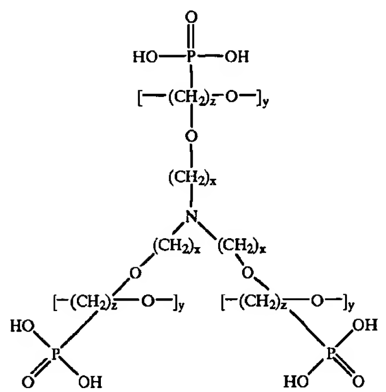
$$R_i'—N—\left((CH_2)_x—O—[(CH_2)_z—O]_y—H\right)_{3-i}$$

where i is either 0 or 1, R' is selected from hydrogen, a C_1 to C_6 alkyl, C_1 to C_6 alkoxy, a cycloalkyl, and an aryl, x and z are integers of 1 to 6, y is an integer from 0 to 2.

Phosphoric acid equivalents such as pyrophosphoric acid (which is equivalent to 105% orthophosphoric acid), tetraphosphoric acid (which is equivalent to 115% orthophosphoric acid) or phosphorus pentoxide (which is equivalent to 138% orthophosphoric acid) also may be used as the phosphoric acid source.

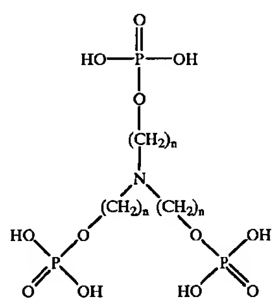
Such alkanol amines are c omm ercially available and include dimethanolamine, diethanolamine, dipropanolamine, dibutanolamine, trimethanolamine, triethanolamine, tripropanolamine, tributanolamine and the alkylene oxide adducts of these alkanolamines such as their ethylene oxide and propylene oxide adducts.

Acidic phosphorus compounds prepared in this manner from trialkanol amines and their adducts have the following formula:



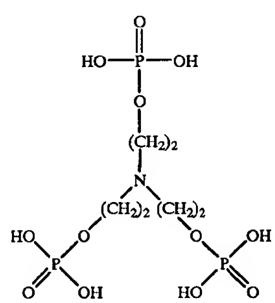
where the oxygen of the alkylenoxy is bonded to the phosphorus and where x, y and z have the same meaning defined above.

A particularly preferred nitrogen-containing, acidic phosphorus compound is the one prepared by neutralizing orthophosphoric acid with trimethanolamine, triethanolamine, tripropanolamine and the like. These preferred compounds have the formula:



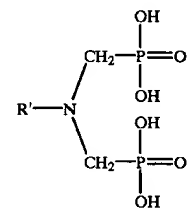
where n is an integer of 1 to 4.

The neutralization adduct of triethanolamine (TEA) and phosphoric acid in an amount of three moles of acid per mole of TEA is known in the art and is commercially available as aminotriethanol phosphate or ATP. For example, ATP is available commercially from P. Chem, Inc., Latexo, Tex. The reaction product is basically considered a triester of TEA and has an acid number of 510–525. ATP has the following formula:

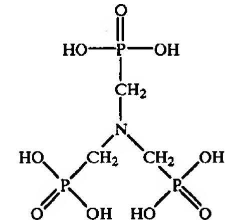


A second class of nitrogen-containing acidic phosphorus compounds useful in the practice of the present invention, generally referred to as phosphonates, can be prepared by reacting phosphorous acid, formaldehyde and ammonia or a primary or secondary amine through a phosphonomethylation reaction among the ammonia or amine, formaldehyde and phosphorous acid. Hydrochloric acid may be added to the reaction mixture to suppress the oxidation of phosphite to phosphate.

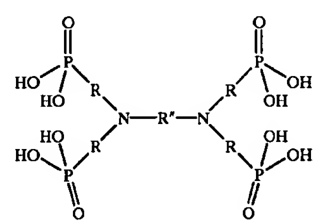
A diphosphonic acid of the formula:



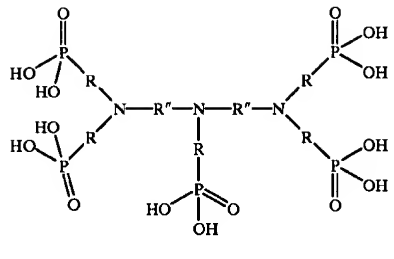
were R' is a monovalent organic radical, preferably a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms such as propyl, isopropyl, butyl, hexyl or 2-hydroxyethyl, can be prepared from a primary amine. An example of a triphosphonic acid is aminotris(methylene-phosphonic acid) (ATMP) made by reacting ammonia, formaldehyde and phosphorous acid. ATMP has the formula:



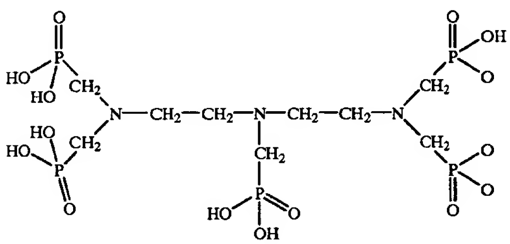
ATMP also is commercially available from P Chem, Inc. Examples of tetraphosphonic acids $R(PO_3H_2)_4$ are the alkylenediaminetetra(methylene-phosphonic acids) of the formula:



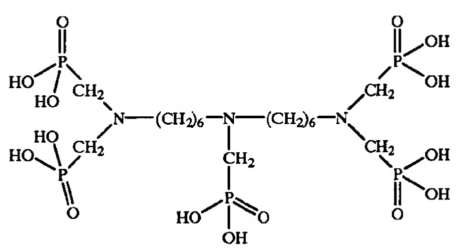
where R" is a divalent organic radical, such as an alkylene group having from 1 to 12 carbon atoms. One example is ethylenediaminetetra(methylene phosphonic acid). Examples of pentaphosphonic acids, $R(PO_3H_2)_5$ are the dialkylenetriaminepenta(methylene phosphonic acids) of the formula:



For example, such pentaphosphonic acids include diethylenetriaminepenta(methylene phosphonic acid) of the formula:



and bis hexamethylenetriaminepenta(methylene phosphonic acid) of the formula:



These nitrogen-containing acidic phosphorus compounds also are commercially available from P Chem as IS-32 and IS-22 respectively.

The acidic phosphorus compounds of the present invention are blended with the melamine compound, preferably a melamine-formaldehyde resin, to form the binder component of the subject composition. Relative proportions of the melamine compound and the acidic phosphorus compound are supplied sufficient to cause the binder to form a hardened coating at a desired rate and at a desired temperature. Normally, the acidic phosphorus compound will be added in an amount of 20 to 100 weight percent based on the weight of the melamine compound, preferably from 30 to 70 weight percent. To facilitate uniform blending of the melamine compound and the acidic phosphorus compound, the acidic phosphorus compound often is added to an aqueous solution of the melamine compound itself as a dilute aqueous solution containing between about 1 to 30% by weight of the acidic phosphorus compound. The solution may also contain additional solvents such as ethylene glycol and n-butanol. Generally, the acidic phosphorus compound is added in an amount to yield a phosphorus content in the ultimately hardened composition of at least about 5% by weight of the coating or impregnating composition, and particularly at least about 10% by weight. Normally, the phosphorus content of the hardened coating will not exceed about 30% by weight.

In one embodiment, an intumescent base composition can be prepared by dissolving melamine in an amount of 10 to 60% by weight of the final composition, preferably 20 to 50%, into a phosphoric acid ester of polyhydroxy compound at an elevated temperature of 100° to 200° C., more usually 120° to 170° C.

The final essential component of the compositions of the present invention is an expandable or swellable graphite flake, for example a graphite compound which contains expansive molecules in the interstitial lattice planes such as an acid, water, halogen, NO_x and/or SO_x and which expand, on heating to a temperature of approximately 150° to 600° C., to multiple times their initial volume (often two orders of magnitude). Mixtures of different types of expandable graphites flakes can also be used. A particularly useful intumescent additive in this regard is GRAFGuard™ expandable graphite flake commercially available from UCAR Carbon Co., Inc.

Graphite is a crystalline form of carbon comprising atoms bonded in flat layered planes with weaker bonds between the planes. By treating particles of graphite, such as natural graphite flake, with an intercalcant of e.g., a solution of sulfuric and nitric acid, the crystal structure of the graphite reacts to form a compound of graphite and the intercalcant. The treated intercalated particles of graphite are known as particles or flakes of "heat expandable graphite" and are commercially available. Upon exposure to high temperature, the particles or flakes of intercalated graphite undergo intumescence and expand in dimension as much as 80 or more times its original volume in an accordion-like fashion in a direction perpendicular to the crystalline planes of the graphite. The exfoliated, i.e. expanded, graphite particles are vermiform in appearance, and are therefore commonly referred to as worms.

A common method for making expandable graphite particles or flakes is described by Shane et al in U.S. Pat. No. 3,404,061 the disclosure of which is incorporated herein by reference. In the typical practice of this method, natural graphite flakes are intercalated by dispersing the flakes in a solution containing an oxidizing agent e.g., a mixture of nitric and sulfuric acid. The intercalation solution contains oxidizing and other intercalating agents known in the art. Examples include those containing oxidizing agents and oxidizing mixtures, such as solutions containing nitric acid, potassium chlorate, chromic acid, potassium permanganate, potassium chromate, potassium dichromate, perchloric acid, and the like, or mixtures, such as for example, concentrated nitric acid and chlorate, chromic acid and phosphoric acid, sulfuric acid and nitric acid, or mixtures of a strong organic acid, e.g. trifluoroacetic acid, and a strong oxidizing agent soluble in the organic acid.

A preferred intercalating agent is a solution of a mixture of sulfuric acid, or sulfuric acid and phosphoric acid, and an oxidizing agent, i.e. nitric acid, perchloric acid, chromic acid, potassium permanganate, hydrogen peroxide, iodic or periodic acids, or the like. Although less preferred, the intercalation solutions may contain metal halides such as ferric chloride, and ferric chloride mixed with sulfuric acid, or a halide, such as bromine as a solution of bromine and sulfuric acid or bromine in an organic solvent.

After the flakes are intercalated, excess solution is drained from the flakes and after washing with water, the intercalated graphite flakes are dried and are expandable upon exposure to a flame for only a few seconds. A preferred commercially available expandable graphite flake product is available from UCAR Carbon Company Inc under the tradename GRAFGuard™. This material has a relatively low "onset"

intumescent temperature which means that it will commence exfoliation generally after only a few seconds exposure to an elevated temperature.

Expansion of expandable graphite is known to have properties which decrease thermal conductivity and provide flame retardation (U.S. Pat. No. 5,176,863 and U.S. Pat. No. 3,574,644).

The expandable graphite flake is added to the binder in an amount sufficient to provide from about 5 to 50 grams of graphite per square foot of area to be treated with the intumescent composition. Generally providing a composition containing the graphite flake in an amount of from 10 to 60 percent by weight should be suitable.

It also may be advantageous under certain circumstances to incorporate additional intumescent adjuvants in the composition, e.g., in order to increase the rising rate of the intumescent layer further or to decrease the density thereof Such intumescent material additives are optionally employed in an amount of up to 200 percent by weight of the graphite flake. Such materials may include polyalcohols, swellable micas, silicates, borates and/or synthetic borosilicates. Such components are usually present in the composition in a minor amount of up to 15% to 30% by weight of the binder solids.

If appropriate, additional binders and the usual fillers can also be used in connection with the present invention. As noted above, such binders may include other resinous compositions such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins. Examples of fillers which can be used are chalk, asbestos, metal powders, metal oxides, metal hydroxides, silicates, carbon, powdered rock, mineral fibers, glass, slags, filter dusts and ashes. The fillers optionally can be added in quantities of, for example, 0 to 30% by weight, preferably 0 to 10% by weight (relative to the binder solids).

Conventional pigments may also be added to the compositions according to the present invention, the total amount thereof usually not exceeding 5 to 50%, particularly 10 to 40% by weight of the total weight of the binder solids. As pigments, all substances which are employed in conventional intumescent compositions and which preferably are of mineral (inorganic) nature are suitable. Examples of such pigments are titania and carbon black.

The aqueous composition of the present invention has particular use as a composition for coating or impregnating a variety of substrates for imparting fire resistant characteristics. Thus, the compositions according to the present invention are preferably present in a form suitable for coating and impregnation purposes, for example as an aqueous or water-containing solution or as a dispersion. The water content of the composition depends on the amount and the nature of the components employed, but preferably is not higher than about 80% by weight of the total composition including water. Normally, the total solids content of the aqueous composition is between about 20 and 90% by weight with compositions having a solids content above about 50% and more usually above 60%, depending on the intended application, generally being preferred. As used herein, the solids content of a composition is measured by the weight loss upon heating a small, 1–5 gram, sample of the composition at about 135° C. for about 2 hours.

Compositions according to the present invention are preferably employed for coating or impregnating articles made of wood (including plywood, OSB, LVL, waferboard, particleboard and the like), plastic (including plastic composites and plastic foams), cellulosic materials (including paper, containerboard, fiberboard and the like) rubber, gypsum board, metal, woven and non-woven glass and ceramic material. The application of the composition may be carried out according to any conventional method, e.g. by spraying, dipping, drawing and brushing. The coating or impregnating process may optionally be repeated several times. The coating thickness and impregnation amount may vary within a wide range, depending on the viscosity of the composition and the substrate to be coated or impregnated. Conventional coating thicknesses range from 0.010 mm to 3 mm.

A particularly preferred application for compositions of the present invention are for treating fiber reinforced plastic (FRP) composites, particularly FRP composites designed for the interior of aircrafts. Such composites typically are based on the use of thermoset resins (e.g., epoxy resins, phenolic resins and the like) and employ a variety of reinforcing fibers (e.g., glass, carbon, Kevlar®) and Nomex® honeycomb. Current FRP panels for the interior walls and ceilings are based on phenolic FRP's because they meet OSU heat release requirements (<65/65) and smoke requirements (<20 @ 4 minutes), per FAA guidelines. FRP panels used in floors are generally based on epoxy resins due to their excellent adhesion with Nomex® and current smoke specifications still allow for the use of epoxy resins (<200 @ 4 minutes). The present invention, as illustrated specifically in Examples 7–11, provides a way for improving the behavior of these epoxy panels, relative to the smoke specifications, to a level similar to the current properties for phenolic FRP's.

The hardening of the composition (e.g., as a coating) is preferably carried out at room temperature, although said hardening can also be carried out at an elevated temperature, often a slightly elevated temperature (preferably up to about 60° C.) will be sufficient, depending on the nature of the components employed.

EXAMPLES

In order to facilitate a more complete understanding of the invention, a number of Examples are provided below. However, the scope of the invention is not limited to specific embodiments disclosed in these Examples, which are for purposes of illustration only. All proportions and quantities referred to in the following examples are by weight unless otherwise stated.

In some of the following examples, the usefulness of various compositions as an intumescent coating was evaluated using the Cone Calorimeter test (ASTM E1354). In this test, heat is applied using a heat flux of a specified intensity generated by a conical radiant heater directed onto an insulated 4 inch by 4 inch test specimen. The parameters which can be monitored include (1) the time to initial ignition of the sample, (2) the heat release rate, (3) the total heat released, (4) the effective heat of combustion and (5) the weight loss of the sample. In the actual tests reported below, the respective compositions were coated onto specimens of plywood board or oriented strand board (OSB). An uncoated plywood specimen exhibited a time to ignition (T_{ig}) of approximately 44 seconds.

In testing the compositions of Comparative Example 8 and Example 8, a modified version of the cone calorimeter test was conducted as follows: a flat, spiral heating element was used to irradiate a sample surface. During the test, samples measuring 4 inch by 4 inch by 1 inch were placed so that the sample surface was 48 mm from the surface of the heating element. Unless otherwise indicated, each sample was heated for 90 seconds. The time to ignition (Tig) and the mass loss were monitored. Unless otherwise indicated, samples that were burning at the conclusion of the heating were removed from the test apparatus and were promptly extinguished in order to calculate the mass loss during the test.

Comparative Example 1

A commercial liquid melamine-formaldehyde/phenol formaldehyde resin marketed by Burke-Hall Coatings (BHC) was mixed with an equal amount of a commercial phosphate ester, Budit-380, commercially available from Chemische Fabrik Budenheim and believed to be a partial ester of a polyol (e.g. pentaerthrytol) and phosphoric acid as disclosed in U.S. Pat. No. 5,387,655. The composition contained at least 10% phosphorus by weight. The mixture then was coated on a 4 inch by 4 inch square of OSB to provide a coating weight of 2 grams (18 grams/ft^2).

Example 1

A commercial liquid melamine-formaldehyde/phenol-formaldehyde resin marketed by Burke-Hall Coatings (BHC) was mixed with an equal amount of the commercial phosphate ester, Budit-380 commercially available from Chemische Fabrik Budenheim, and with an equal amount of GRAFGuard™ expandable graphite flake marketed commercially by UCAR Carbon Company, Inc. The composition contained about 8% phosphorus by weight. The mixture then was coated on a 4 inch by 4 inch square of OSB to provide a coating weight of 3 grams (27 grams/ft^2).

Comparative Example 2

A commercial liquid melamine-formaldehyde/phenol-formaldehyde resin marketed by Burke-Hall Coatings (BHC) was mixed with an equal amount aminotriethanol-phosphate acidic phosphorus curing agent (ATP). The composition contained about 6% phosphorus by weight. The mixture then was coated on a 4 inch by 4 inch square of OSB to provide a coating weight of 2 grams (18 grams/ft^2).

Example 2

A commercial liquid melamine-formaldehyde/phenol-formaldehyde resin marketed by Burke-Hall Coatings (BHC) was mixed with an equal amount aminotriethanol-phosphate acidic phosphorus curing agent (ATP) and with an equal amount of GRAFGuard™ expandable graphite flake marketed commercially by UCAR Carbon Company, Inc. The composition contained about 5% phosphorus by weight. The mixture then was coated on a 4 inch by 4 inch square of OSB to provide a coating weight of 3 grams.

Cone Calorimeter Tests (CCT)

The OSB specimens coated with the compositions of Comparative Examples 1 and 2 and Examples 1 and 2 were tested for their performance in the CCT. The composition test results are presented below in Table 1. Addition of GRAFGuard™ expandable graphite flake to the composition of Comparative Example 2 gave a 54 percent increase in Tig. The height of intumescent produced was 0.5 inches and the expanded flake appeared to be bonded by the intumescent material derived from the binder/coating system. This synergism is highly unexpected from the standpoint of coating durability and fire resistance enhancement.

TABLE 1

CONE CALORIMETER TEST RESULTS OBTAINED OVER A TEN MINUTE PERIOD

Example	Ext. Ht. Flux, (kW/m^2)	T_{ig}, (sec)	Peak Heat Release Rate (kW/m^2)	Average Heat Release Rate (kW/m^2)	Initial Mass, (g)	Mass Loss, (g)	Mass Loss, (%)
Comp. Ex. 1	35	203	67	44	87.5	27.6	32
Ex. 1	35	443	37	17	88.9	12.4	14
Comp. Ex. 2	35	644	<10	4	82.9	9.1	11
Ex. 2	35	990	<10	3	88.8	5.3	6

ABBREVIATIONS:
T_{ig} Time to ignition
HRR Heat Release Rate
THR Total Heat Released
Eff. Hc Effective Heat of Combustion

Comparative Example 3

A commercial powdered (spray-dried) melamine-formaldehyde resin marketed by Cytec as Aerotru-19 (34.7 wt. %) was mixed with water (10.5 wt. %), n-butanol (2.4 wt. %), a commercial liquid acid curable PF resin from Georgia-Pacific Resins, Inc. (GP637D52) (2.4 wt. %) and aminotriethanolphosphate acidic phosphorus curing agent (ATP) (50 wt. %). The composition contained about 8% phosphorus by weight. The mixture then was applied as a coating in an amount of about 27 grams of aqueous coating per square foot on 4 ft.×8 ft. panels of OSB and fiberboard. The coated products were tested (E-84 Tunnel Test). The test results are reported in Table 2.

Example 3

A commercial powdered (spray-dried) melamine-formaldehyde resin marketed by Cytec as Aerotru-19 (21.9 wt. %) was mixed with water (6.4 wt. %), n-butanol (1.5 wt. %), a commercial liquid acid curable PF resin (GP637D52) (1.5 wt. %), aminotriethanolamine acidic phosphorus curing agent (ATP) (29.5 wt. %) and GRAFGuard™ expandable graphite flake (30.3 wt. %). The composition contained about 6% phosphorus by weight. The mixture then was applied as a coating in an amount of about 27 grams of aqueous coating per square foot on 4 ft.×8 ft. panels of OSB and fiberboard. The coated products were tested (E-84 Tunnel Test). The test results are reported in Table 2.

TABLE 2

E-84 Tunnel Test Results for Coated OSB and Sound Deadening Fiberboard Panels

Example	Panel	Flame Spread Index	Smoke Development
Comp. Ex. 3	OSB	10	100
Ex. 3	OSB	5	20
Comp. Ex. 3	Fiberboard	20	185
Ex. 3	Fiberboard	10	40

Example 4

Using the compositions of Comparative Example 3 and Example 3, Underwriter Laboratories small scale fire tests (an alcohol flame impingement with 45° oriented sample) were conducted on hardboard. Table 3 illustrates the aque-

ous coating weight on the hardboard samples and the test results. An uncoated control board also was tested.

TABLE 3

Underwriter Laboratory Small Scale Fire Test Results for Coated Hardboard			
Example	Uncured Coating Wt. (g/ft.^{2})	Burn Area (square inches)	Burn Time (seconds)
Comp. Ex. 3	14	12.95	0
Ex. 3	14	0	0
Ex. 3	28	0	0
Control (no coating)	—	15.31	60

Comparative Example 5

An intumescent binder was prepared by initially preparing a pentaerythritol phosphate ester by mixing 30 parts by weight pentaerythritol with 10 parts by weight phosphoric acid (100%) and forming a melt. Thereafter, an additional 5 parts by weight of P_2O_5 was added to the melt. After heating for 5 minutes at 150° C. a clear melt is obtained. Finally, 30 parts by weight of melamine powder is added to the phosphate ester melt over 20 minutes with heating. The resulting mixture was applied as produced (100% solids by weight) in an amount of about 18 grams/ft^2 onto an OSB substrate (4"×4"×7/16") to provide an intumescent coating. The coated board was subjected to CCT at a radiant heat flux of 35 kW/m^2 for ten minutes. The results are presented in Table 4.

Example 5

An intumescent composition also was prepared by adding GRAFGuard™ expandable graphite flake to the binder of Comparative Example 5 and the composition was coated onto an OSB panel (4"×4"×7/16") at a loading of 9 g/ft^2 GRAFGuard™ expandable graphite flake and 18 g/ft^2 of the intumescent composition described in Comparative Example 5. This coated panel also was subjected to CCT at a radiant heat flux of 35 kW/m^2 for ten minutes. The results are presented in Table 4.

Comparative Example 6

An intumescent binder was prepared by mixing 25% by weight of the binder of Comparative Example 5, 25% by weight of a 30% solution of aminotriethanolphosphate and 50% by weight of the BHC resin mixture. The binder was coated onto an OSB panel (4"×4"×7/16") in an amount of 18 grams/ft^2 and subjected to CCT as above. The results are presented in Table 4.

Example 6

Using the binder composition of Comparative Example 6, a coating slurry was prepared by adding an amount of GRAFGuard™ expandable graphite flake equal in amount to the BHC resin in the original mixture. The composition was applied as a coating onto an OSB panel in an amount of 27 grams/ft^2 and subjected to CCT as above. The results are presented in Table 4.

TABLE 4

SUMMARY OF CONE CALORIMETER TEST RESULTS FOR A TEN MINUTE PERIOD				
Example No.	Time to Ignition (sec.)	Peak Heat Release Rate (kw/m^2)	Average Heat Release	Mass Loss (% @ 10 min.)
Plywood Control	44	207	103	75
Comp. Ex. 5	165	68	17	31
Ex. 5	>600	5	<1	8
Comp. Ex. 2	644	<10	4	11
Ex. 2	990	<10	3	6
Comp. Ex. 1	203	67	44	32
Ex. 1	443	37	17	14
Comp. Ex. 6	643	—	2	11
Ex. 6	742	—	3	7

Data reported at end of 10 minute time period for Peak Heat Release, Average Heat Release and Mass Loss.

Comparative Example 7

A commercial liquid melamine-formaldehyde resin marketed by Georgia-Pacific Resins, Inc. GP-542D59 (50 parts) was mixed with an acidic phosphorus curing agent (ATP) (25 parts) and the binder of Comparative Example 5 (25 parts). The mixture then was coated on a 4 inch by 4 inch square of OSB to provide a coating weight of 2 grams (18 grams/ft^2). The results are presented in Table 5.

Example 7

Using the binder composition of Comparative Example 7, a coating slurry was prepared by adding an amount of GRAFGuard™ expandable graphite flake equal to the melamine-formaldehyde resin in the original mixture. The composition was applied as a coating onto an OSB panel in an amount of 3 grams (27 grams/ft^2) and subjected to CCT as above. The results are presented in Table 5.

TABLE 5

Summary of Cone Calorimeter Test Results Obtained Over a Ten Minute Period											
Example	Ext. Ht. Flux, kW/m^2	Tig, s	Peak HRR, kW/m^2	Time to Peak, s	Ave. HRR Ign. + 60s kW/m^2	THR, kJ	Eff. Hc, MJ/kg	Ave. Spec. Extn. Area, m^2/kg	Initial Mass, g	Mass Loss, g	Mass* Loss, %
Comp. Ex. 7	35	337	64.5	452	17.55	119	6.2	60.0	84.1	19.4	23.1
Ex. 7	35	425	31.4	585	19.73	51	4.3	5.4	88.9	12.0	13.5

ABBREVIATIONS:
Tig Time to ignition
HRR Heat Release Rate
THR Total Heat Released
Eff. Hc Effective Heat of Combustion

Comparative Example 8

An aqueous resin composition useful for producing an intumescent coating was prepared by mixing 66 grams of a commercial liquid melamine-formaldehyde/phenol-formaldehyde resin marketed by Burke-Hall Coatings (BHC) with 61 grams of deionized water and 66 grams of aminotriethanolphosphate acidic phosphorus curing agent (ATP) with stirring until a colorless, water-clear solution was obtained.

Example 8

An aqueous resin composition containing GRAFGuard™ expandable graphite flakes useful for producing an intumescent coating was prepared by taking 67 grams of the aqueous resin composition of Comparative Example 8 and adding 23 grams of expandable graphite.

Heat Resistance Testing

The intumescent behaviors of hardened coatings of the Comparative Example 8 and Example 8 compositions were examined by brushing the respective aqueous compositions onto 4-inch samples of foam, with the samples then placed in a 70° C. oven for seventy minutes to harden the coating. Two types of semi-rigid polyurethane foam were used to evaluate the effectiveness of hardened intumescent compositions of the aqueous resin compositions. Foam A comprised a polyurethane foam without any additional flame retardant additive, while Foam B comprised a polyurethane foam containing a halogenated flame retardant additive. The coating weights reported below exclude the amount of deionized water used in preparing the aqueous compositions.

An uncoated sample of Foam A (Control A), placed in the laboratory test apparatus and heated, began to burn vigorously after 3 seconds with the evolution of large amounts of black smoke. The sample continued burning when removed from the test fixture after 30 seconds, and was completely consumed after an additional 60 seconds. Mass loss was 100%.

An uncoated sample of Foam B (Control B) containing a halogenated flame retardant additive was placed in the test apparatus and heated for 90 seconds. The sample began to burn vigorously after 3 seconds with the evolution of large amounts of black smoke. The sample continued burning when removed from the test fixture after 90 seconds, and was completely consumed in an additional 30 seconds. Mass loss of the foam was 100%.

A sample of semi-rigid polyurethane Foam A was coated with 3.9 grams of the composition of Comparative Example 8 (35 grams/ft^2). The sample was oven-dried, then placed in the test apparatus and heated for 90 seconds. The sample began to burn vigorously after 7 seconds with the evolution of black smoke. The foam sample lost 85% of its original mass by the end of the test.

A sample of semi-rigid polyurethane Foam A was coated with 3.8 grams of the composition of Example 8 (34 grams/ft^2). The dried sample was placed in the test apparatus and heated for 90 seconds. The graphite began to expand within 20 seconds, insulating the surface of the foam. There was no sustained ignition and no black smoke generated during the test. The expanded layer containing the graphite worms showed good rigidity and adhesion to the foam by virtue of the co-expansion of the graphite with the intumescent resin. There was some decomposition of the foam under the intumescent layer. Foam mass loss was only 15%.

A sample of semi-rigid polyurethane Foam B was coated with 3.1 grams of the composition of Comparative Example 8 (28 grams/ft^2). The dried sample was placed in the test apparatus and heated for 90 seconds. The sample began to burn vigorously after 4 seconds with the evolution of extremely thick, black smoke. The foam sample loss 100% of its original mass by the end of the test.

A sample of semi-rigid polyurethane Foam B was coated with 4.5 grams of the composition of Example 8 (41 grams/ft^2). The dried sample was placed in the test apparatus and heated for 90 seconds. The graphite was fully expanded within 22 seconds, insulating the surface of the foam with about a 0.75-inch layer of expanded graphite worms and resin. The expanded layer containing the graphite worms showed good rigidity and adhesion to the foam by virtue of the co-expansion of the graphite with the intumescent resin. There was no ignition or "flashing" (momentary, unsustained ignition), and no black smoke generated during the test. There was some decomposition of the foam under the intumescent layer during the test. Foam mass loss was only 13%.

The results of the foregoing tests are summarized in Table 6.

TABLE 6

FOAM TYPE	INTUMESCENT COATING	TIME TO IGNITION (Sec.)	FOAM MASS LOSS (%)	OBSERVED SMOKE
A	NONE	3	100	HEAVY
A	COMP. EX. 8	7	85	HEAVY
A	EXAMPLE 8	>90	15	NONE
B	NONE	3	100	HEAVY
B	COMP. EX. 8	4	100	HEAVY
B	EXAMPLE 8	>90	13	NONE

It will be understood that while the invention has been described in conjunction with specific embodiments thereof, the foregoing description and examples are intended to illustrate, but not limit the scope of the invention. Other aspects, advantages and modifications will be apparent to those skilled in the art to which the invention pertains, and these aspects and modifications are within the scope of the invention, which is limited only by the appended claims.

What is claimed is:

1. An intumescent composition comprising a hardened binder of a melamine compound and an acidic phosphorus compound, said binder containing expandable graphite flakes.

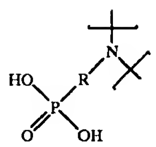
2. An aqueous composition suitable for producing a fire resistant coating on a substrate, said composition comprising a hardenable binder of a melamine compound and an acidic phosphorus compound, said binder containing expandable graphite flakes.

3. A method for imparting fire resistance to a substrate comprising treating said substrate with an aqueous composition comprising a hardenable binder of a melamine compound and an acidic phosphorus compound, said binder containing expandable graphite flakes.

4. A fire resistant article comprising a substrate coated or impregnated with a hardened aqueous composition, said composition comprising a hardenable binder of a melamine compound and an acidic phosphorus compound, said binder containing expandable graphite flakes.

5. The invention of claim **1**, **2**, **3** or **4** wherein the melamine compound is an acid curable melamine-formaldehyde resin.

6. The invention of claim **5** wherein the phosphorus compound contains one or more moieties of the following formula:

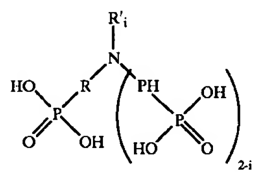


where R is selected from the group consisting of a C_1 to C_6 alkylene radical, a C_3 to C_7 cycloalkylene radical, an arylene radical and a divalent radical of the formula:

$$-(CH_2)_x-O-[(CH_2)_z-O]_y-$$

where x and z are integers of 1 to 6, and y is an integer from 0 to 2 and wherein the divalent radical is bonded to the phosphorous atom of said moieties through the terminal oxygen atom of said radical.

7. The invention of claim **1**, **2** **3** or **4** wherein the phosphorus compound is a compound of the following formula:



where R is selected from the group consisting of a C_1 to C_6 alkylene radical, a C_3 to C_7 cycloalkylene radical, an arylene radical and a divalent radical of the formula:

$$-(CH_2)_x-O-[(CH_2)_z-O]_y-$$

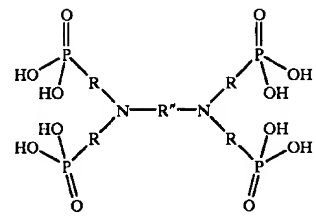
where x and z are integers of 1 to 6, and y is an integer from 0 to 2 and wherein the divalent radical is bonded to the phosphorous atoms of said compound through the terminal oxygen atom of said radical where i is 0 or 1, and R' is selected from hydrogen, a C_1 to C_6 alkyl, a C_1 to C_6 alkoxy, a cycloalkyl and an aryl.

8. The invention of claim **7** wherein the melamine compound is a melamine-formaldehyde resin prepared by reacting melamine and formaldehyde in an aqueous reaction medium under an alkaline condition at a melamine to formaldehyde mole ratio in the range of 1:1 to 6:1.

9. The invention of claim **8** wherein the phosphorus compound is selected from the group consisting of aminotriethanol phosphate and aminotris(methylene-phosphonic acid).

10. The invention of claim **1**, **2** **3** or **4** wherein the phosphorus compound is a compound of the following formula (II):

(II)



where R is selected from the group consisting of a C_1 to C_6 alkylene radical, a C_3 to C_7 cycloalkylene radical, an arylene radical and a divalent radical of the formula:

$$-(CH_2)_x-O-[(CH_2)_z-O]_y-$$

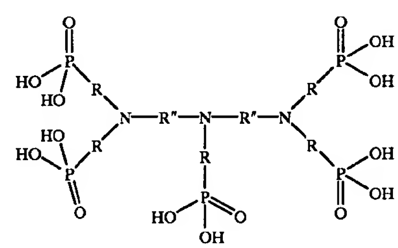
were x and z are integers of 1 to 6, and y is an integer from 0 to 2 and wherein the divalent radical is bonded to the phosphorous atoms of said compound through the terminal oxygen atom of said radical and where R" is a divalent organic radical.

11. The invention of claim **10** wherein the melamine compound is a melamine-formaldehyde resin prepared by reacting melamine and formaldehyde in an aqueous reaction medium under an alkaline condition at a melamine to formaldehyde mole ratio in the range of 1:1 to 1:6.

12. The invention of claim **11** wherein the phosphorus compound is ethylene diamine tetra(methylene phosphonic acid).

13. The invention of claim **1**, **2** **3** or **4** wherein the phosphorus compound is a compound of the following formula (III):

(III)



where R is selected from the group consisting of a C_1 to C_6 alkylene radical, a C_3 to C_7 cycloalkylene radical, an arylene radical and a divalent radical of the formula:

$$-(CH_2)_x-O-[(CH_2)_z-O]_y-$$

where x and z are integers of 1 to 6, and y is an integer from 0 to 2 and wherein the divalent radical is bonded to the phosphorous atoms of said compound through the terminal oxygen atom of said radical and where R" is a divalent organic radical.

14. The invention of claim **13** wherein the melamine compound is a melamine-formaldehyde resin prepared by reacting melamine and formaldehyde in an aqueous reaction medium under an alkaline condition at a melamine to formaldehyde mole ratio in the range of 1:1 to 1:6.

15. The invention of claim **14** wherein the phosphorus compound is selected from the group consisting of

diethylenetriaminepenta(methylene phosphonic acid) and bis hexamethylenetriaminepenta(methylene phosphonic acid).

16. The invention of claim 1, 2 3 or 4 wherein the phosphorus compound is a partial phosphate esters of phosphoric acid and a polyhydroxy compound.

17. The invention of claim 16 wherein the melamine compound is a melamine-formaldehyde resin prepared by reacting melamine and formaldehyde in an aqueous reaction medium under an alkaline condition at a melamine to formaldehyde mole ratio in the range of 1:1 to 1:6.

18. The invention of claim 17 wherein the phosphorus compound is the reaction product of phosphoric acid and a polyhydroxy compound selected from the group consisting of pentacrythritol, glycerol, trimethylol propane and mixtures thereof.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,228,914 B1
DATED : May 8, 2001
INVENTOR(S) : Brian M. Ford et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,
Item [56], **References Cited,**
-- OTHER DOCUMENTS International Search Report for PCT/US98/27530 dated April 2, 1999 -- has been inserted.

Column 6,
Line 58, "c omm ercially" has been replaced with -- commercially --.

Column 19, claim 7,
Line 32, "PH" has been replaced with -- R --.

Signed and Sealed this

Twentieth Day of November, 2001

Attest:

Nicholas P. Godici

NICHOLAS P. GODICI

Attesting Officer *Acting Director of the United States Patent and Trademark Office*

US005965268A

United States Patent [19]

Sastri et al.

[11] Patent Number: 5,965,268

[45] Date of Patent: Oct. 12, 1999

[54] **CARBON-BASED COMPOSITES DERIVED FROM PHTHALONITRILE RESINS**

[75] Inventors: **Satya B. Sastri**, Greenbelt, Md.; **James P. Armistead**, Fairfax; **Teddy M. Keller**, Fairfax Station, both of Va.

[73] Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, D.C.

[21] Appl. No.: **09/105,087**

[22] Filed: **Jun. 26, 1998**

[51] **Int. Cl.**[6] **B32B 9/00**; C01B 31/08

[52] **U.S. Cl.** **428/408**; 428/366; 428/367; 428/378; 428/379; 428/446; 428/698; 428/699; 428/704; 428/908.8; 501/98; 501/99; 427/122; 252/502; 252/503; 264/29.7

[58] **Field of Search** 428/408, 366, 428/367, 378, 379, 446, 698, 699, 704, 908.8; 501/98, 99; 427/122; 252/502, 503; 264/29.7

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,408,035 10/1983 Keller 528/183
4,409,382 10/1983 Keller 528/173
4,587,325 5/1986 Keller 528/172
5,389,441 2/1995 Keller 428/395
5,645,219 7/1997 Miks et al. 239/265.11
5,686,027 11/1997 Olsen et al. 264/29.7
5,759,688 6/1998 Lee et al. 428/408

OTHER PUBLICATIONS

Buckley, John D. and Edie, Dan D., ed., *Carbon–Carbon Materials and Composites,* Noyes Publications, Park Ridge, NJ (1993), Chapter 5.

Primary Examiner—Richard Weisberger
Attorney, Agent, or Firm—Thomas E. McDonnell; Ralph T. Webb

[57] **ABSTRACT**

A carbon-based composite is made by the steps of

(1) impregnating a fibrous material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing the product of step (2) to form the carbon-based composite. The carbon-based composite may be made with only one cycle of the steps (1), (2), and (3).

19 Claims, No Drawings

CARBON-BASED COMPOSITES DERIVED FROM PHTHALONITRILE RESINS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to carbon-based composites, and in particular to carbon-based composites derived from phthalonitrile resins.

2. Description of the Related Art

Carbon-based composites are materials that are composed of a fibrous reinforcement in a carbonaceous or graphitic matrix. A filler or coating may also be included to impart specialized properties.

As used in this application, the term "carbon-based composite" refers generally to any composite having a fibrous reinforcement in a carbonaceous or graphitic matrix. The terms "carbon/carbon composite" or "carbon-carbon composite" refer to a carbon-based composite wherein the fibrous reinforcement comprises carbon fiber.

Carbon-carbon composites are lightweight materials, with densities ranging from about 1.36 to about 2.00 g/cm^3, depending on the precursors used for their production. Carbon-based composites may have greater density, depending on the density of the particular fibrous reinforcement used. Carbon-based composites possess great thermal stability in non-oxidizing environments and may be coated with an oxidation-resistant coating for use in oxidizing environments.

Typically, carbon-based composites are formed by impregnating a fibrous material with an organic resin and then heating or pyrolyzing the mixture to carbonizing temperatures. For carbon/carbon composites, the carbon fiber material is typically derived from polyacrylonitrile (PAN), rayon, or petroleum pitch. Silicon carbide, metal, glass or ceramic fibers may be used to fabricate other types of carbon-based composites.

First-generation matrix materials for carbon-based composites were derived from phenolic and phenolic-furfuryl alcohol resins. These resins have the disadvantage that when they are cured and pyrolyzed to form a carbon-based composite, they generate volatiles, which create voids in the composite. To eliminate the voids and to produce a carbon-based composite with an acceptable density, multiple steps of impregnation and carbonization are required. The process of making a carbon-based composite with these types of resins is therefore time-consuming and expensive. With some currently used carbon precursor materials, it can take 6 to 8 months of repeated impregnation and pyrolysis steps to make a thick, complex carbon/carbon structure. More recently, other materials such as liquid (mesophase) pitch have been used as the matrix material. These materials typically have a high viscosity, which makes the process of impregnating a fibrous material more difficult. Other processes such as chemical vapor deposition/chemical vapor infiltration (CVD/CVI) of volatile hydrocarbon compounds have been used to achieve higher densities. However, with chemical vapor methods, carbon tends to deposit preferentially on the surface of the fibrous material and a thorough penetration of a thick fiber matrix is difficult to achieve.

A variety of methods and materials for making carbon/carbon composites are described in numerous publications and patents including, for example, the following: Buckley, John D. and Edie, Dan D., ed., *Carbon-Carbon Materials and Composites,* Noyes Publications, Park Ridge, N.J. (1993); Delmonte, John, *Technology of Carbon and Graphite Fiber Composites,* Van Nostrand Reinhold Company, New York, N.Y. (1981); Schmidt et al, "Evolution of Carbon-Carbon Composites (CCC)" SAMPE Journal, Vol.32, No. 4, July/August 1996, pp 44–50; "Expanding Applications Reinforce the Value of Composites" High Performance Composites 1998 Sourcebook; U.S. Pat. No. 3,914,395 to Finelli, et al; U.S. Pat. No. 4,178,413 to DeMunda; U.S. Pat. No. 5,061,414 to Engle; U.S. Pat. No. 4,554,024 to Zimmer, et al; and U.S. Pat. No. 5,686,027 to Olsen, et al. All of the above patents and publications are incorporated herein by reference.

A method for making a silicon carbide fiber reinforced carbon composite is described in U.S. Pat. No. 5,759,688 to Lee et al, incorporated herein by reference.

Phthalonitrile monomers and resins have been used for making thermoset polymers. Phthalonitriles have the advantage that they are easily processed and can be cured without generating volatile by-products. Various phthalonitrile resins are described, for example, in U.S. Pat. No. 3,730,946, U.S. Pat. No. 3,763,210, U.S. Pat. No. 3,787,475, U.S. Pat. No. 3,869,499, U.S. Pat. No. 3,972,902, U.S. Pat. No. 4,209,458, U.S. Pat. No. 4,223,123, U.S. Pat. No. 4,226,801, U.S. Pat. No. 4,234,712, U.S. Pat. No. 4,238,601, U.S. Pat. No. 4,259,471, U.S. Pat. No. 4,304,896, U.S. Pat. No. 4,307,035, U.S. Pat. No. 4,315,093, U.S. Pat. No. 4,351,776, U.S. Pat. No. 4,408,035, U.S. Pat. No. 4,409,382, U.S. Pat. No. 4,410,676, U.S. Pat. No. 5,003,039, U.S. Pat. No. 5,003,078, U.S. Pat. No. 5,004,801, U.S. Pat. No. 5,132,396, U.S. Pat. No. 5,159,054, U.S. Pat. No. 5,202,414, U.S. Pat. No. 5,208,318, U.S. Pat. No. 5,237,045, U.S. Pat. No. 5,242,755, U.S. Pat. No. 5,247,060, U.S. Pat. No. 5,292,854, U.S. Pat. No. 5,304,625, U.S. Pat. No. 5,350,828, U.S. Pat. No. 5,352,760, U.S. Pat. No. 5,464,926, U.S. Patent Application by Satya B. Sastri and Teddy M. Keller for "FIBER-REINFORCED PHTHALONITRILE COMPOSITE CURED WITH LOW-REACTIVITY AROMATIC AMINE CURING AGENT" filed Oct. 2, 1997 and U.S. Patent Application by Satya B. Sastri and Teddy M. Keller for "PHTHALONITRILE THERMOSET POLYMERS AND COMPOSITES CURED WITH HALOGEN-CONTAINING AROMATIC AMINE CURING AGENTS" filed Oct. 2, 1997. All of these patents and applications are incorporated herein by reference.

U.S. Pat. No. 4,587,325, incorporated herein by reference, describes a conductive phthalonitrile polymer formed by heating a mixture of a diether-linked bisorthonitrile (phthalonitrile) monomer and an amine to a temperature above 450° C. U.S. Pat. No. 5,389,441, incorporated herein by reference, describes a fiber-reinforced composite formed by combining a fiber sized with a cured or partially cured phthalonitrile coating and a polymeric matrix. U.S. Pat. No. 5,645,219, incorporated herein by reference, describes the use of phthalonitrile resin as a matrix material in a fiber-reinforced ablative composite. The patent describes thermogravimetric testing of cured neat phthalonitrile resin samples by heating to 900° C. Methods of making fiber-reinforced thermoset composites based on phthalonitrile resins are described in Sastri et al, "Phthalonitrile-Carbon Fiber Composites" Polymer Composites, December 1996, Vol. 17, No. 6, pp 816–822 and Sastri et al "Phthalonitrile-Glass Fabric Composites", Polymer Composites, February 1997, Vol. 18, No. 1, pp 48–54, the disclosures of which are incorporated herein by reference.

SUMMARY OF THE INVENTION

It has now been discovered that carbon-based composites can be made by using phthalonitrile resins as precursors for forming the carbonaceous matrix material of the composite.

Accordingly, the present invention is directed to a method of making a carbon-based composite comprising the steps of

(1) impregnating a fibrous material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing the product of step (2) to form the carbon-based composite.

In another aspect, the invention is directed to a carbon-based composite made by a process comprising the steps of

(1) impregnating a fibrous material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing product of step (2) to form the carbon-based composite.

In another aspect, the invention is directed to a method of making a carbon/carbon composite comprising the steps of

(1) impregnating a carbon fiber material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing the product of step (2) to form the carbon/carbon composite.

In another aspect the invention is directed to a carbon/carbon composite made by a process comprising the steps of

(1) impregnating a carbon fiber material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing product of step (2) to form the carbon/carbon composite.

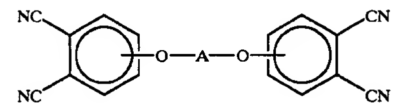
By using phthalonitrile resins as precursors for forming the carbonaceous matrix material of a carbon-based composite or a carbon/carbon composite, it is possible to make a dense, void-free composite in a single cycle of impregnation, cure and pyrolysis. Multiple steps of impregnation, cure and pyrolysis that are necessary with other resin systems to achieve an acceptable density are not required.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

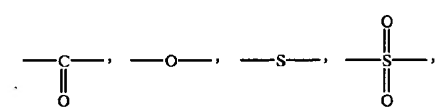
The present invention relates to a carbon-based composite and a method of making the composite by the steps of (1) impregnating a fibrous material with a phthalonitrile thermoset polymer precursor, (2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and (3) pyrolyzing the product of step (2) to form the carbon-based composite.

As used herein, the term "phthalonitrile thermoset polymer precursor" refers to any material or mixture that may be cured to form a phthalonitrile thermoset polymer. Included in this definition, for example, are phthalonitrile monomers, mixtures of different phthalonitrile monomers, mixtures of phthalonitrile monomers and one or more curing agents, and partially cured B-staged prepolymers.

The phthalonitrile monomer may be any phthalonitrile monomer, such as are described, for example, in U.S. Pat. No. 3,730,946, U.S. Pat. No. 3,763,210, U.S. Pat. No. 3,787,475, U.S. Pat. No. 3,869,499, U.S. Pat. No. 3,972,902, U.S. Pat. No. 4,209,458, U.S. Pat. No. 4,223,123, U.S. Pat. No. 4,226,801, U.S. Pat. No. 4,234,712, U.S. Pat. No. 4,238,601, U.S. Pat. No. 4,259,471, U.S. Pat. No. 4,304,896, U.S. Pat. No. 4,307,035, U.S. Pat. No. 4,315,093, U.S. Pat. No. 4,351,776, U.S. Pat. No. 4,408,035, U.S. Pat. No. 4,409,382, U.S. Pat. No. 4,410,676, U.S. Pat. No. 5,003,039, U.S. Pat. No. 5,003,078, U.S. Pat. No. 5,004,801, U.S. Pat. No. 5,132,396, U.S. Pat. No. 5,159,054, U.S. Pat. No. 5,202,414, U.S. Pat. No. 5,208,318, U.S. Pat. No. 5,237,045, U.S. Pat. No. 5,242,755, U.S. Pat. No. 5,247,060, U.S. Pat. No. 5,292,854, U.S. Pat. No. 5,304,625, U.S. Pat. No. 5,350,828, U.S. Pat. No. 5,352,760,U.S. Pat. No. 5,464,926, U.S. Patent Application by Satya B. Sastri and Teddy M. Keller for "FIBER-REINFORCED PHTHALONITRILE COMPOSITE CURED WITH LOW-REACTIVITY AROMATIC AMINE CURING AGENT" filed Oct. 2, 1997 and U.S. Patent Application by Satya B. Sastri and Teddy M. Keller for "PHTHALONITRILE THERMOSET POLYMERS AND COMPOSITES CURED WITH HALOGEN-CONTAINING AROMATIC AMINE CURING AGENTS" filed Oct. 2, 1997. Preferably, the phthalonitrile monomer is a compound of the formula:



wherein A is any divalent organic radical. More preferably, A is selected from the group consisting of substituted or unsubstituted phenyl radicals, polyphenyl radicals, polyphenoxy radicals, fused aromatic poly-ring radicals and radicals of the general form —Ar—Z—Ar— where Ar is a substituted or unsubstituted aromatic group and Z is



any alkylene of up to six carbon atoms, any halogenated alkylene of up to six carbon atoms, an imide-containing group or a connecting bond. By the word "substituted", it is meant that any known substituent could be attached to the aromatic moiety. Substituents include but are not limited to halogens, chalcogens, and organic radicals such as phenyl, alcohol, carboxyl, carbonyl, or aliphatic groups of less than 10 carbon atoms.

The curing agent may be any curing agent useful in promoting the polymerization of the phthalonitrile monomer under reactive conditions, such as temperatures above the melting point of the monomer. The curing agent should be stable and nonvolatile at elevated temperatures. Preferably, the curing agent is selected from the group of curing agents consisting of aromatic amines, phenols, inorganic acids, strong organic acids, metals, metallic salts and combinations thereof. Most preferably, the curing agent is an aromatic amine.

A B-staged prepolymer is made by partially polymerizing a phthalonitrile monomer or a mixture of monomers, preferably in the presence of a curing agent. Upon cooling, the B-staged prepolymer is typically a frangible solid which can be pulverized into a powder.

As used herein, the terms "fibers" and "fibrous material" are used interchangeably herein to refer to any type of reinforcing fiber useful in creating fiber-reinforced composites. Examples of useful fibers and fibrous materials are given in U.S. Pat No. 4,894,286 and U.S. Pat. No. 5,002,750, the entire disclosures of which are hereby incorporated

herein by reference. Preferably, the fibers are carbon fibers or silicon carbide fibers. Carbon fibers are preferably fibers that are derived from polyacrylonitrile (PAN), rayon, or petroleum pitch. The fibers may also be metal, glass or ceramic.

The selection of a fibrous material for forming a carbon-based composite or carbon-carbon composite is influenced by the desired density for the final product. For example, fibrous material based on rayon typically has a density of about 1.42 g/cm^3, fibrous material based on polyacrylonitrile (PAN) typically has a density of about 1.76 to 1.94 g/cm^3, fibrous material based on mesophase petroleum pitch typically has a density of about 2.01 g/cm^3. The corresponding carbon-carbon composites have a density from about 1.36 to about 2.00 g/cm^3. Greater densities may be achieved by using inorganic fibrous material such as metal or glass fibers.

The fibrous material can be in any physical form useful in creating fiber-reinforced composites including, for example, woven fabrics, nonwoven mats, or tow. The fibrous material may be a fibrous preform with a shape corresponding to a particular desired end product.

The steps of impregnating the fibrous material with a phthalonitrile thermoset polymer precursor and of curing the mixture to form a fiber-reinforced thermoset polymer may by carried out by any method known in the art for creating fiber-reinforced thermoset polymers. In particular, conventional methods of prepreg consolidation, filament winding, resin transfer molding and resin infusion molding may be used. Techniques for making composite structures are described in numerous sources, including, for example, in the following patents and publications incorporated herein by reference: Sastri et al, "Phthalonitrile-Carbon Fiber Composites" Polymer Composites, December 1996, Vol. 17, No.6, pp 816–822; Sastri et al "Phthalonitrile-Glass Fabric Composites", Polymer Composites, February 1997, Vol.18, No.1, pp 48–54; Buckley, John D. and Edie, Dan D., ed., *Carbon-Carbon Materials and Composites,* Noyes Publications, Park Ridge, N.J. (1993); Delmonte, John, *Technology of Carbon and Graphite Fiber Composites,* Van Nostrand Reinhold Company, New York, N.Y. (1981); Schmidt et al, "Evolution of Carbon-Carbon Composites (CCC)" SAMPE Journal, Vol. 32, No. 4, July/August 1996, pp 44–50; "Expanding Applications Reinforce the Value of Composites" High Performance Composites 1998 Sourcebook; U.S. Pat. No. 3,914,395 to Finelli, et al; U.S. Pat. No. 4,178,413 to DeMunda; U.S. Pat. No. 5,061,414 to Engle; U.S. Pat. No. 4,554,024 to Zimmer, et al; and U.S. Pat. No. 5,686,027 to Olsen, et al, and U.S. Pat. No. 5,744,221 to Crane, et al. As used herein, the term "impregnating" a fibrous material means saturating the fibrous material with the phthalonitrile thermoset polymer precursor, such as is typically done in the conventional methods of resin transfer molding and resin infusion molding or other methods. Typically, the step of curing the mixture of the fibrous material and the phthalonitrile thermoset polymer precursor will include heating the mixture to a temperature at or below about 375° C.

The fiber-reinforced thermoset polymer is pyrolyzed to form the carbon-based composite by heating the fiber-reinforced thermoset polymer in an inert atmosphere for a sufficient time and at a sufficient temperature to carbonize the thermoset polymer. Preferably, the temperature range for the pyrolysis is between 450° C. and 1000° C., most preferably between 500° C. and 850° C. The length of time that the fiber-reinforced thermoset polymer is kept in the temperature range above 450° C. depends on the size and thickness of the polymer, and is preferably over 100 hours.

In making carbon-based composites, it is important to avoid creating defects or disruptions that may be caused by thermal stress or the evolution of volatiles during the pyrolyzing process. The evolution of volatiles is greatly reduced by the use of phthalonitriles as in the present invention, but can be reduced still further by controlling the heating rate of the fiber-reinforced thermoset polymer in the temperature range above 400° C. Thermal stress, which is caused by a difference in the coefficient of thermal expansion between the thermoset polymer and the fibrous material is also reduced by controlling the heating rate. Preferably, the heating above 400° C. is carried out at a rate of less than 20° C./min, most preferably at a rate of less than 1° C./min.

The steps of impregnation, cure and pyrolysis may be carried out as a single continuous process, for example, by impregnating the fibrous material with the phthalonitrile thermoset polymer precursor while heating the mixture up through the temperature range where curing occurs and then continuing to heat the mixture up to the temperature range where carbonization occurs. Alternatively, the method of the invention may be carried out in distinct stages. For example, a two-dimensional fibrous material may be impregnated with the phthalonitrile thermoset polymer precursor to form a prepreg which can be stored for later use. Then subsequently, prepregs may be stacked to form a laminate and heated to curing and carbonizing temperatures.

An important feature of the present invention is that a carbon-based composite having an acceptable density for structural applications and having no visible voids may be created by carrying out only one cycle of the steps of impregnation, cure and pyrolysis. Multiple steps of impregnation, cure and pyrolysis such as are required when other resin systems are used (see, for example, Buckley et al, supra, pp 9–11, which describes repeated cycles of impregnation and carbonization), are not necessary when a phthalonitrile thermoset polymer precursor is used.

Having described the invention, the following examples are given to illustrate specific applications of the invention, including the best mode now known to perform the invention. These specific examples are not intended to limit the scope of the invention described in this application.

EXAMPLES

Example 1

Formation of phthalonitrile composite from 4,4'-bis (3,4-dicyanophenoxy)biphenyl monomer, an amine catalyst and unidirectional IM7-carbon fiber

4,4'-Bis(3,4-dicyanophenoxy)biphenyl monomer (1000 g, 2.27 moles) was melted at 275° C. in a 2000 ml reaction kettle equipped with a mechanical stirrer. The temperature was lowered to 265° C. and 1,3-bis(3-aminophenoxy) benzene (21 g, 0.072 mole) was added in small quantities with vigorous stirring. After 15 minutes of reaction time, the melt was quenched to room temperature to obtain a B-staged phthalonitrile resin or a prepolymer. The prepolymer was powdered finely and used in the solution impregnation process to formulate a phthalonitrile/carbon prepreg. Unsized Hercules IM7-12K carbon fiber with a density of 1.77 g/cc was used to make a unidirectional tape with 37 weight % resin. A composite panel was fabricated by consolidation of eight plies of the prepreg (9"x11") in an autoclave by heating for 1 hour at 250° C. and 3 hours at 325° C. under 200 psi pressure. The composite panel was postcured under an inert atmosphere of nitrogen for an additional 8 hours each at 325, 350 and 375° C. prior to carbonization.

Example 2

Formation of phthalonitrile composite from 4,4'-bis (3,4-dicyanophenoxy)biphenyl monomer, an amine catalyst and T-650/35 carbon fabric

4,4'-Bis(3,4-dicyanophenoxy)biphenyl monomer (1000 g, 2.27moles) was melted at 275° C. in a 2000 ml reaction kettle equipped with a mechanical stirrer. The temperature was lowered to 265° C. and 1,3-bis(3-aminophenoxy) benzene (18 g, 0.062 mole) was added in small quantities with vigorous stirring. After 15 minutes of reaction time, the melt was quenched to room temperature to obtain a B-staged phthalonitrile resin or a prepolymer. The prepolymer was powdered finely and used in composite processing by resin infusion method. Amoco T650/35, 8 harness satin weave carbon fabric with UC 309 sizing and a density of 1.77 g/cc was used. Eight plies of the fabric (6"×6") were stacked above 49 g of prepolymer distributed evenly on a 6"×6" glass weave. A composite panel was processed in an autoclave by heating for 1 hour at 250° C. and 3 hours at 325° C. under 200 psi pressure. The composite panel was post-cured under an inert atmosphere of nitrogen for an additional 8 hours each at 325, 350 and 375° C. prior to carbonization.

Example 3

Formation of neat resin sample based on 1,3 bis(3, 4-dicyanophenoxy)benzene and 1,3 bis(3-aminophenoxy)benzene as the curing agent

1,3 Bis(3,4-dicyanophenoxy)benzene (2.3 g, 6.2 mmoles) was melted in an aluminum planchet on a hot plate at 220° C. The melt was degassed for 2 hours at 220° C. and 0.044 g (0.15 mmole) of 1,3 bis(3-aminophenoxy)benzene (APB) was added to the melt with stirring. After a 15 minutes dwell at 220° C., the melt was degassed for an additional 10 minutes and quenched to room temperature. The sample was cured in an oven by heating at 260° C. for 12 hours, 325° C. for 12 hours, 350° C. for 8 hours and 375° C. for 8 hours under an inert atmosphere of argon.

Example 4

Formation of neat resin sample based on 1,3 bis(3, 4-dicyanophenoxy)benzene and bis[4-(4-aminophenoxy)phenyl]sulfone as the curing agent

1,3 Bis(3,4-dicyanophenoxy)benzene (2.3 g, 6.2 mmoles) was melted in an aluminum planchet on a hot plate at 220° C. The melt was degassed for 2 hours at 220° C. and 0.068 g (0.15 mmole) of bis[4-(4-aminophenoxy)phenyl]sulfone (BAPS) was added to the melt with stirring. After a 15 minutes dwell at 220° C., the melt was degassed for an additional 10 minutes and quenched to room temperature. The sample was cured in an oven by heating at 260° C. for 12 hours, 325° C. for 12 hours, 350° C. for 8 hours and 375° C. for 8 hours under an inert atmosphere of argon.

Example 5

Formation of neat resin sample based on 1,3 bis(3, 4-dicyanophenoxy)biphenyl and 1,3 bis(3-aminophenoxy)benzene as the curing agent

1,3 Bis(3,4-dicyanophenoxy)biphenyl (2.73 g, 6.2 mmoles) was melted in an aluminum planchet on a hot plate at 250° C. The melt was degassed for 2 hours at 250° C. and 0.044 g (0.15 mmole) of 1,3 bis(3-aminophenoxy)benzene (APB) was added to the melt with stirring. After a 15 minutes dwell at 250° C., the melt was degassed for an additional 10 minutes and quenched to room temperature. The sample was cured in an oven by heating at 260° C. for 12 hours, 325° C. for 12 hours, 350° C. for 8 hours and 375° C. for 8 hours under an inert atmosphere of argon.

Example 6

Formation of neat resin sample based on 2,2-bis[4-(3,4-dicyanophenoxy) phenyl]propane and 1,3 bis (3-aminophenoxy)benzene as the curing agent

2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]propane (2.99 g, 6.2 mmoles) was melted in an aluminum planchet on a hot plate at 220° C. The melt was degassed for 2 hours at 220° C. and 0.044 g (0.15 mmole) of 1,3 bis(3-aminophenoxy) benzene (APB) was added to the melt with stirring. After a 15 minutes dwell at 220° C., the melt was degassed for an additional 10 minutes and quenched to room temperature. The sample was cured in an oven by heating at 260° C. for 12 hours, 325° C. for 12 hours, 350° C. for 8 hours and 375° C. for 8 hours under an inert atmosphere of argon.

Example 7

Carbonization

Phthalonitrile composite samples (1"×1") from examples 1 and 2, and small pieces (0.5–1 g) of neat resins from examples 3, 4, 5 and 6 were dried in a vacuum oven at 110° C. for 2 hours and cooled in a desiccator to record the initial weights. The samples were placed in a retort furnace and flushed with argon for 12 hours before the heating cycle began. The following heating program was used: (1) heat from 25 to 325° C. at 5° C./min, (2) hold at 325° C. for 1 hour, (3) heat from 325 to 850° C. over a period of 120 hours (0.07° C./min), (4) hold at 850° C. for 4 hours and (5) cool to room temperature at 1° C./min. The observed weight loss upon carbonization of neat resin samples in examples 3–6 were 25.1%, 25.4%, 23.3% and 20.3%, respectively. The unidirectional and fabric-based composite lost 9.0% and 7.4% weight, respectively. The densities of the pyrolyzed composite samples were determined by water displacement technique (ASTM D 792). The density of the IM7-based unidirectional composite is 1.65 g/cc and that of fabric-based composite is 1.60 g/cc. The density of the resultant carbon/carbon composite is highly dependent on the fiber density; therefore, higher density composites may be obtained through the use of pitch-based fibers that have a density of 2.01 g/cc (as opposed to 1.77 g/cc for IM7 and T-650 fibers).

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method of making a carbon-based composite comprising the steps of

(1) impregnating a fibrous material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing the product of step (2) to form the carbon-based composite.

2. The method of claim 1 wherein said method comprises only one cycle of the steps (1), (2) and (3).

3. The method of claim 1 wherein the step (3) of pyrolyzing the product of step (2) is carried out by heating the

product of step (2) at a temperature of between about 450° C. and about 1000° C. for a period of time sufficient to carbonize the fiber-reinforced thermoset polymer.

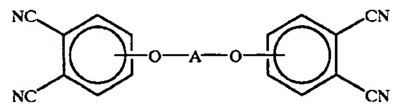
4. The method of claim **3** wherein the product of step (2) is kept at a temperature in the range of about 450° C. to about 1000° C. for at least 100 hours.

5. The method of claim **3** wherein the product of step (2) is heated at a rate of less than 20° C. per minute.

6. The method of claim **3** wherein the product of step (2) is heated at a rate of less than 1° C. per minute.

7. The method of claim **1** wherein the phthalonitrile thermoset polymer precursor is a mixture of a phthalonitrile monomer and a curing agent.

8. The method of claim **7** wherein the phthalonitrile monomer is a compound of the formula:



wherein A is a divalent organic radical.

9. The method of claim **8** wherein A is selected from the group consisting of substituted or unsubstituted phenyl radicals, polyphenyl radicals, polyphenoxy radicals, fused aromatic poly-ring radicals and radicals of the general form —Ar—Z—Ar— where Ar is a substituted or unsubstituted aromatic group and Z is

$$-\underset{\underset{O}{\|}}{C}-,\quad -O-,\quad -S-,\quad -\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-,$$

an alkylene of up to six carbon atoms, a halogenated alkylene of up to six carbon atoms, an imide-containing group or a connecting bond.

10. The method of claim **7** wherein the curing agent is selected from the group of curing agents consisting of aromatic amines, phenols, inorganic acids, strong organic acids, metals, metallic salts and combinations thereof.

11. The method of claim **1** wherein the phthalonitrile thermoset polymer precursor is a partially cured B-staged phthalonitrile prepolymer.

12. The method of claim **1** wherein the fibrous material comprises inorganic fibers selected from the group consisting of silicon carbide fibers, glass fibers, metal fibers and ceramic fibers.

13. A carbon-based composite made by a process comprising the steps of

(1) impregnating a fibrous material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing product of step (2) to form the carbon-based composite.

14. The carbon-based composite of claim **13**, wherein said process comprises only one cycle of the steps (1), (2) and (3).

15. A method of making a carbon/carbon composite comprising the steps of

(1) impregnating a carbon fiber material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing the product of step (2) to form the carbon/carbon composite.

16. The method of claim **15** wherein said method comprises only one cycle of the steps (1), (2) and (3).

17. The method of claim **15** wherein the carbon fiber material is selected from the group consisting of fibers derived from polyacrylonitrile, fibers derived from rayon and fibers derived from petroleum pitch.

18. A carbon/carbon composite made by a process comprising the steps of

(1) impregnating a carbon fiber material with a phthalonitrile thermoset polymer precursor,

(2) curing the product of step (1) to form a fiber-reinforced thermoset polymer and

(3) pyrolyzing product of step (2) to form the carbon/carbon composite.

19. The carbon/carbon composite of claim **18**, wherein said process comprises only one cycle of the steps (1), (2) and (3).

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US005968653A

United States Patent [19]

Coppella et al.

[11] **Patent Number: 5,968,653**

[45] **Date of Patent: Oct. 19, 1999**

[54] **CARBON-GRAPHITE/SILICON CARBIDE COMPOSITE ARTICLE**

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[73] Assignee: **The Morgan Crucible Company, plc**, Windsor, United Kingdom

[21] Appl. No.: **08/585,147**

[22] Filed: **Jan. 11, 1996**

[51] **Int. Cl.**[6] **B32B 9/00**

[52] **U.S. Cl.** **428/408**; 428/306.6; 428/312.6; 428/323; 428/328; 428/446; 428/448; 428/614; 428/627; 428/698; 428/699; 501/90; 501/99; 501/100; 501/126; 427/113; 427/226; 427/249; 427/250; 264/44; 264/63

[58] **Field of Search** 428/328, 408, 428/698, 699, 323, 614, 545, 446, 448, 627, 367, 306.6, 312.6; 427/249, 250, 229, 226, 376.7, 383.5, 376.6, 228, 343, 113; 501/90, 88, 99, 87, 127, 126, 100; 264/63, 44; 228/121, 124.5

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[57] **ABSTRACT**

A carbon-graphite/silicon carbide composite article is provided. The composite article includes a carbon-graphite body intimately bonded to a dense silicon carbide body by a transition/bonding region which links the two bodies. The transition/bonding region between the carbon-graphite body and the silicon carbide body typically includes a layer rich in silicon metal and a small silicon carbide/silicon metal/carbon graphite area where some of the carbon-graphite from the carbon-graphite body has been converted to silicon carbide. The carbon-graphite body may also include a variety of impregnants.

17 Claims, 6 Drawing Sheets

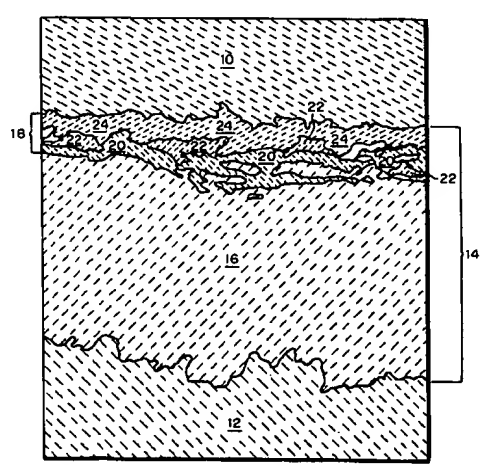

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FIG. 1

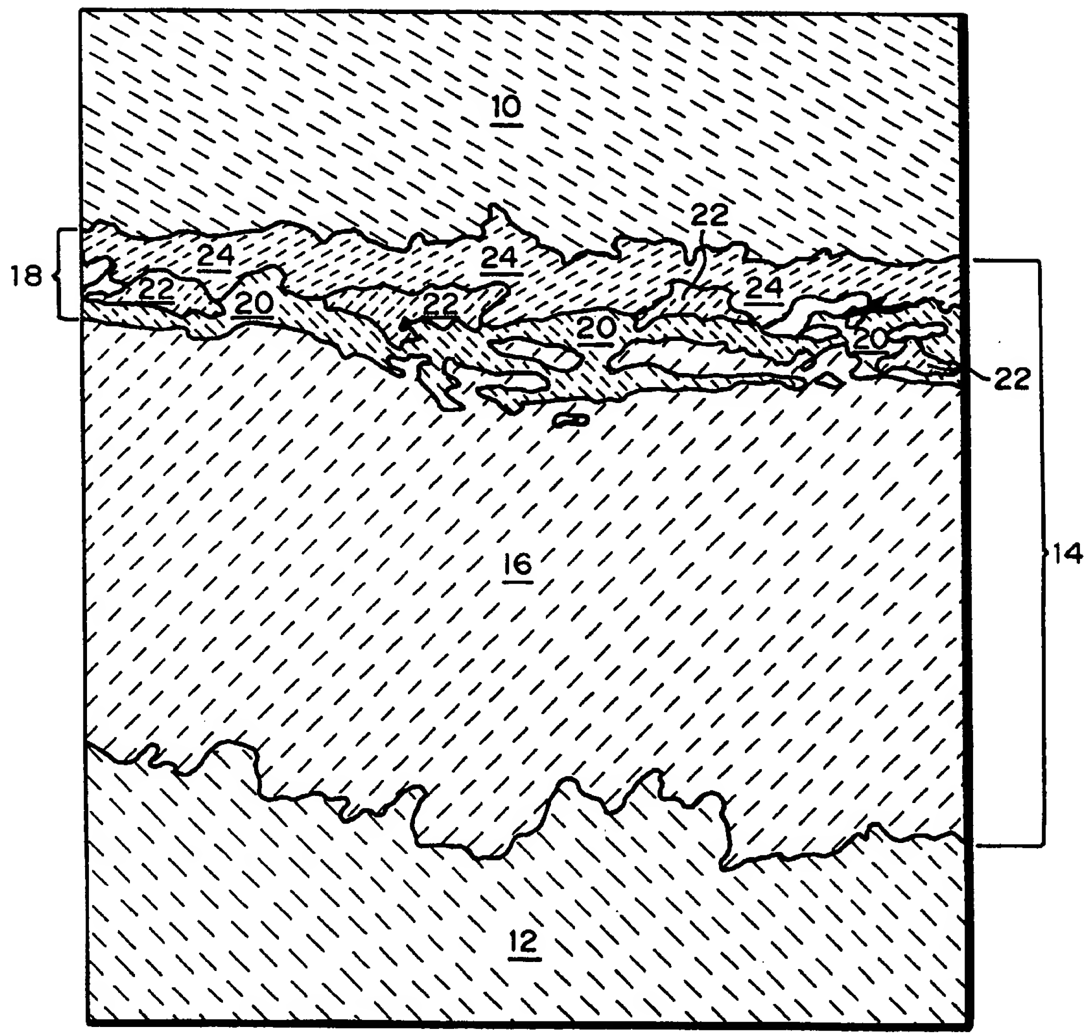


FIG.2A

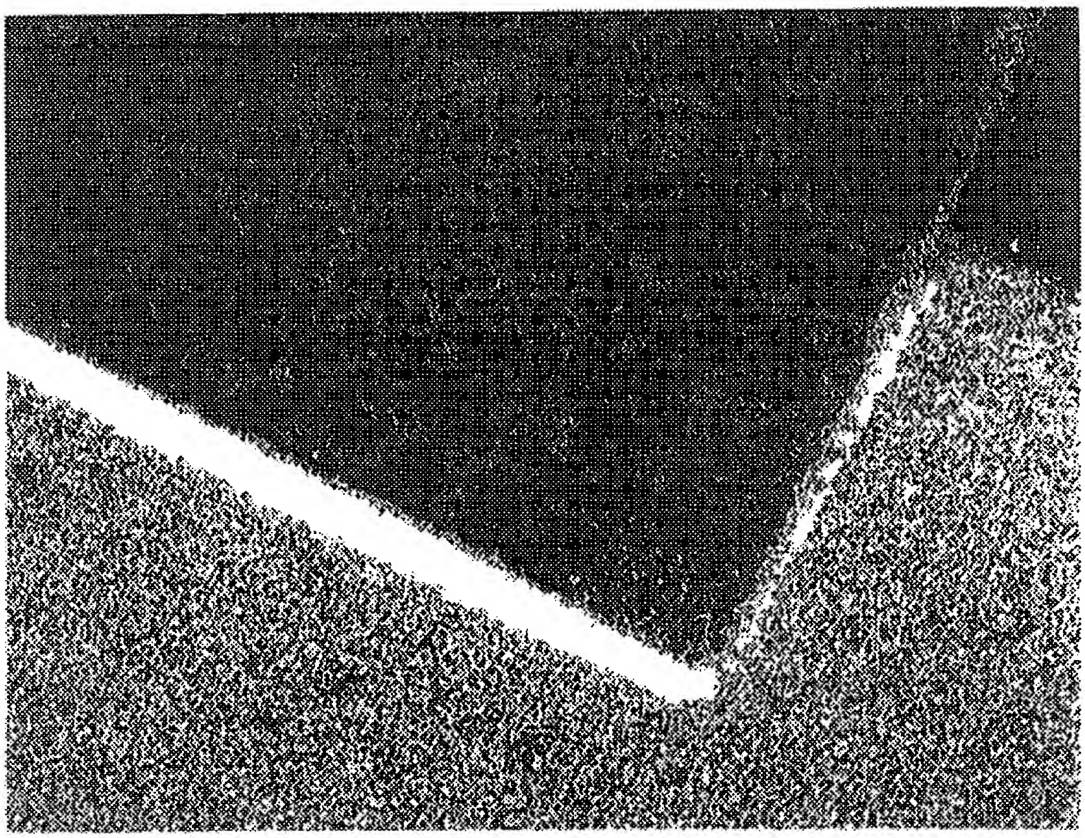


FIG. 2B

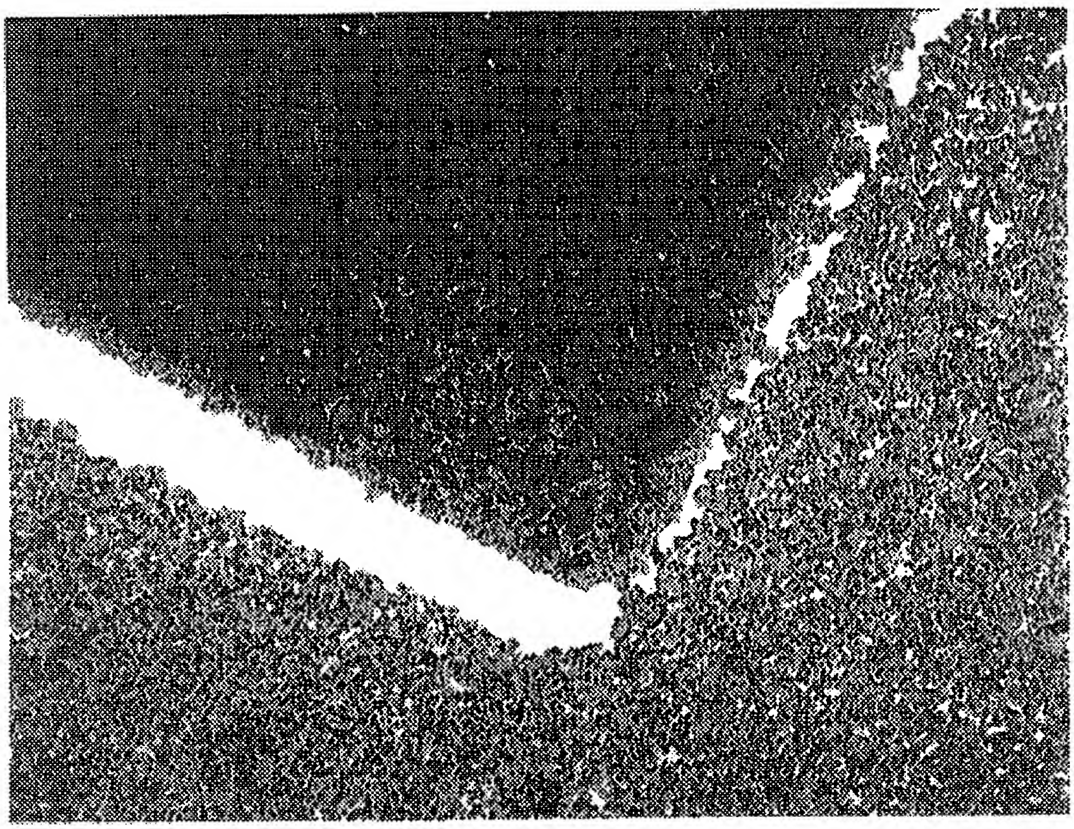


FIG.2C

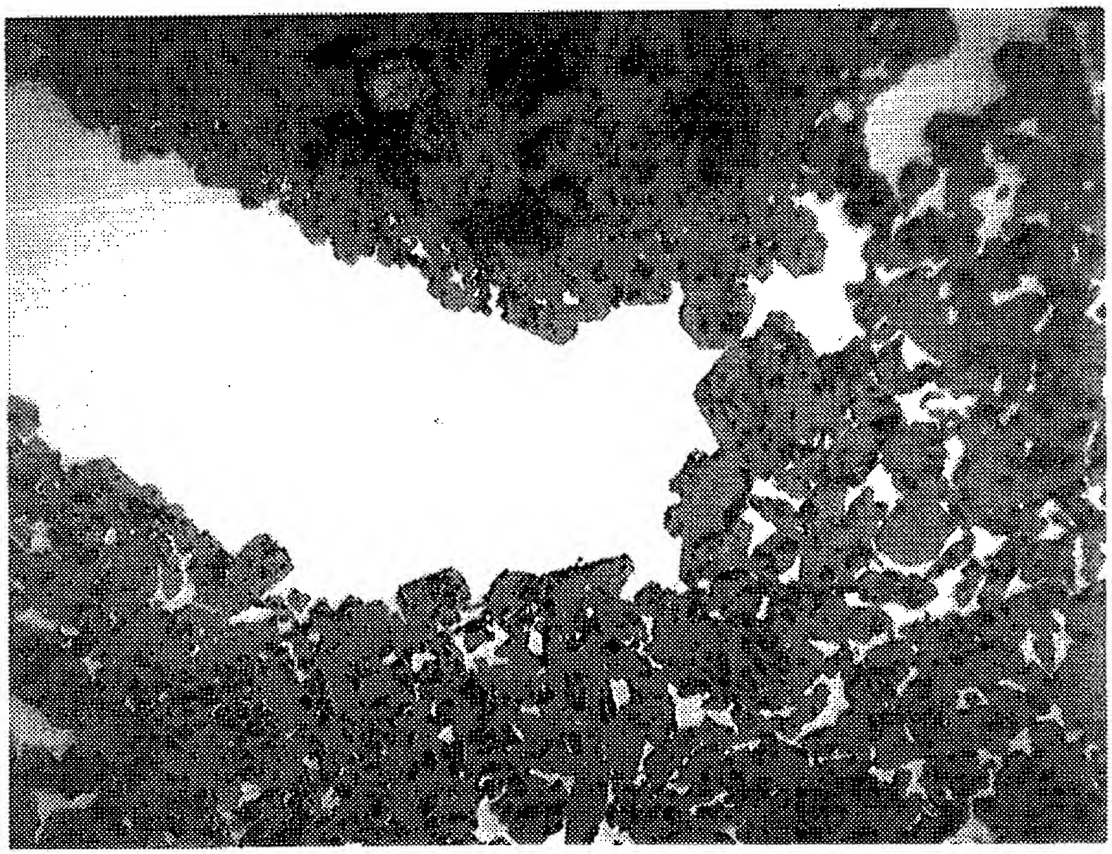


FIG. 3

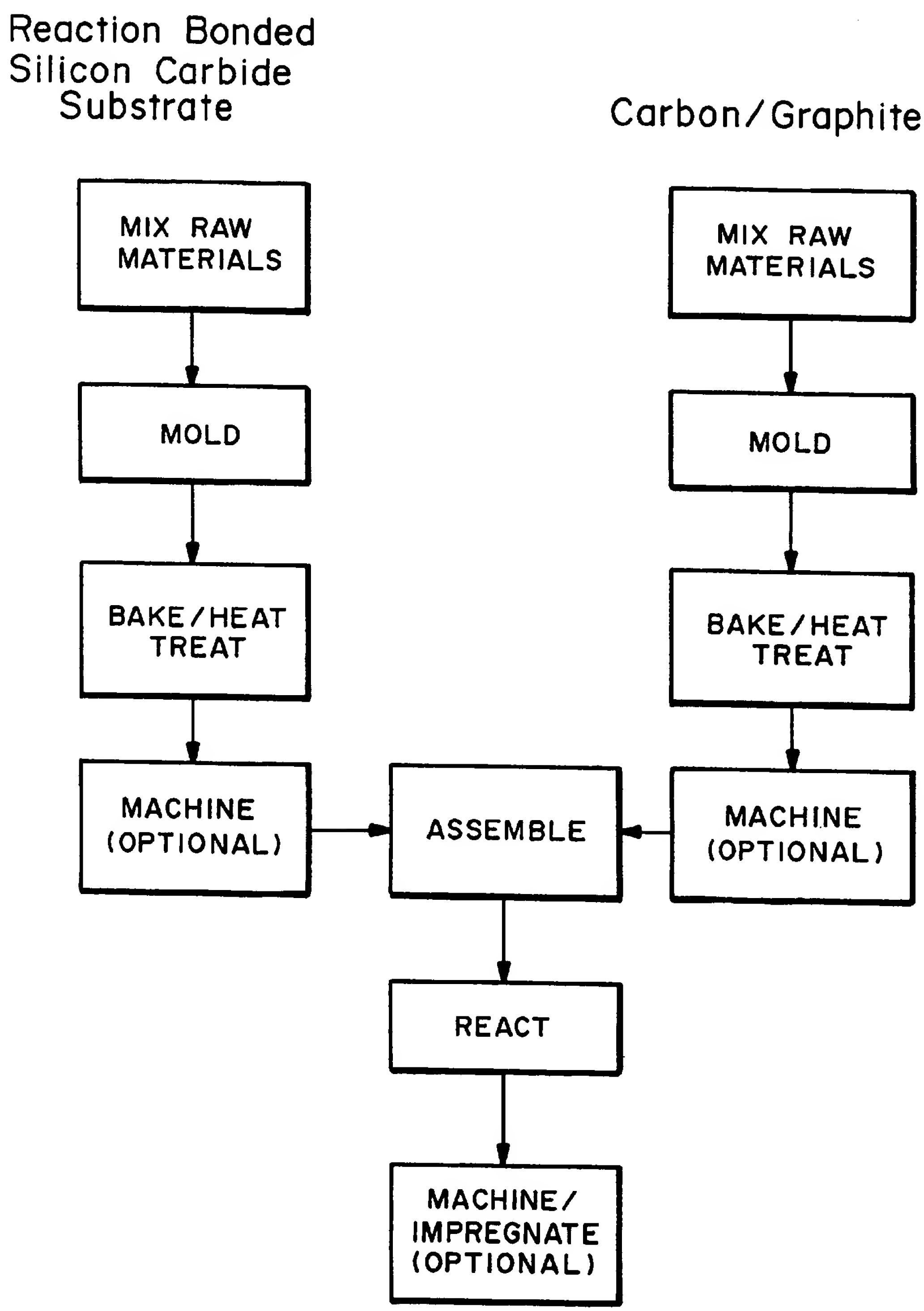

Reaction Bonded
Silicon Carbide
Substrate
Carbon/Graphite
MIX RAW MATERIALS
MOLD
BAKE/HEAT TREAT
MACHINE (OPTIONAL)
MIX RAW MATERIALS
MOLD
BAKE/HEAT TREAT
MACHINE (OPTIONAL)
ASSEMBLE
REACT
MACHINE/ IMPREGNATE (OPTIONAL)

FIG. 4A

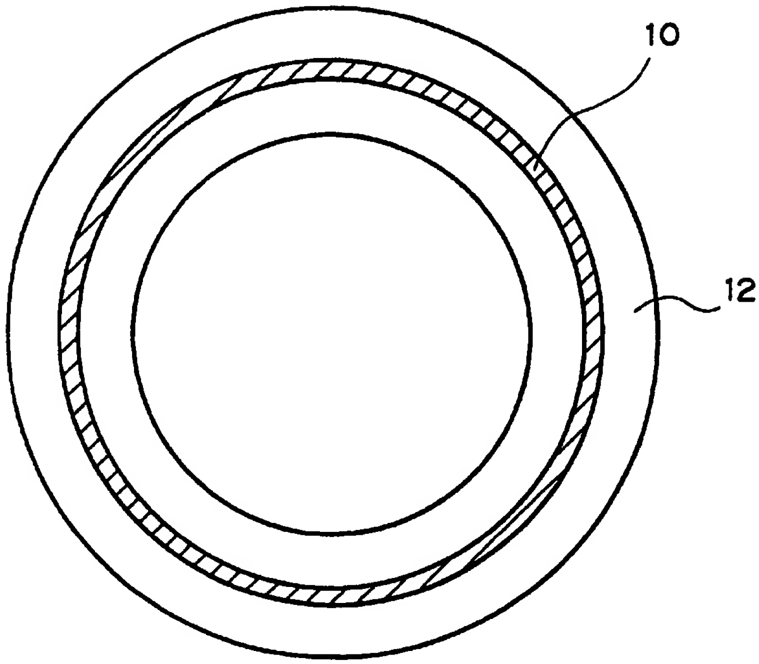
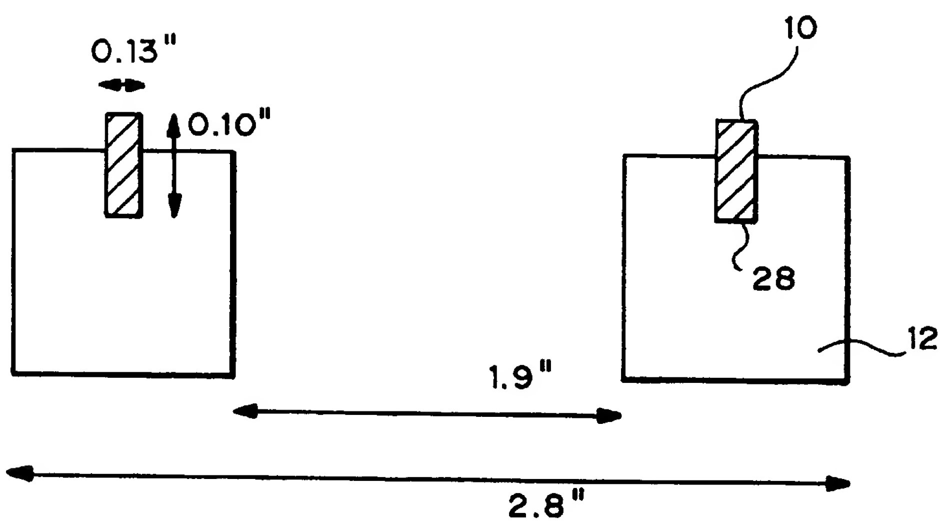


FIG. 4B



CARBON-GRAPHITE/SILICON CARBIDE COMPOSITE ARTICLE

FIELD OF THE INVENTION

This invention relates to the field of carbon-graphite/silicon carbide composite articles and more particularly to composite articles comprised of carbon-graphite bodies bonded to silicon carbide bodies.

BACKGROUND OF THE INVENTION

In the area of friction and seal components for demanding applications, seal designs are often compromised by the need to choose among materials which have exclusive and independent benefits, and sometimes conflicting characteristics. The seal designs are often compromised in material selection because, while some materials have beneficial properties in certain respects, the materials may have disadvantages, or less desirable characteristics, in other respects. For example, some seal materials (i.e. carbon/graphites) have self-lubricating properties, and therefore perform very well in dry run and process upset conditions. Typically, such materials also have a low modulus of elasticity, which allows the materials to deflect against the mating face of a seal (which is usually a high modulus ceramic). However, because of the low modulus, such materials lack strength and stiffness. Further, the materials also lack high oxidation resistance.

Other seal materials (e.g. self-sintered silicon carbides) have superior strength and a high modulus of elasticity, which provides the stiffness necessary to give the entire seal assembly stability and strength, and have high oxidation resistance. However, such materials are not self-lubricating. Therefore, the materials have poor dry running and/or process upset response characteristics.

SUMMARY OF THE INVENTION

The present invention includes a carbon-graphite/silicon carbide composite article. The composite article includes a carbon-graphite body intimately bonded to a dense silicon carbide body by a transition/bonding region which links the two bodies. The transition/bonding region between the carbon-graphite body and the silicon carbide body typically includes a layer rich in silicon metal and a small silicon carbide/silicon metal/carbon graphite region where some of the carbon-graphite from the carbon-graphite body has been converted to silicon carbide. The carbon-graphite body, which typically would be used as a tribological material in a seal or bearing application, may also include a variety of impregnants to further enhance the tribological, physical or chemical characteristics of the body, or to eliminate the porosity of the body for seal applications.

In the production of the composite article of the present invention, the carbon-graphite body and the silicon carbide body are first manufactured separately. The two materials are then assembled and reacted to convert the silicon carbide body into a dense body and to produce the transition/bonding region which provides intimate adhesion between the previously separate bodies. Some overlap of part of the cross sections of the bodies is provided (i.e. so that one of the bodies is partially embedded in, or is keyed into, the other) to allow sufficient adhesion and shear strength to withstand application forces. The overlap may, for example, be provided by fitting part of one body into a race or groove formed in the other. After reaction of the bodies and formation of the composite article, the carbon-graphite body, which is porous, can then be impregnated with an impregnant to further enhance the tribological, physical or chemical characteristics of the body, or to eliminate the porosity of the body.

The resultant composite article of the present invention is a stiff, strong and self-lubricating article particularly suitable for seal and bearing members. The unique characteristics of the composite article combine the superior strength, high modulus of elasticity and high oxidation resistance of silicon carbide with the lower modulus and self-lubricating characteristics of mechanical carbon-graphite. Further, in seal applications, because the silicon carbide body is separated from the rubbing surface of the material by the carbon-graphite body, the running temperature of the composite article is reduced in both normal and adverse conditions from that of a plain, e.g. reaction bonded, silicon carbide body. Thus, the opportunity for thermal shock, as well as catastrophic failure of seal/bearing assemblies, is reduced.

Further, the resultant article of the present invention is unique in that it does not compromise the structure of the silicon carbide by introducing flaws, such as graphite inclusions, into the silicon carbide which would weaken the structure of the silicon carbide body and lower its modulus of elasticity and strength.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more fully understood from the following detailed description considered in conjunction with the accompanying drawings, in which:

FIG. **1** is a detailed cross-sectional schematic representation of a carbon-graphite/silicon carbide composite article of the present invention;

FIGS. **2A**, **2B**, and **2C** are photomicrographs, taken at 50×, 100×, and 400×, respectively, of the composite article of FIG. **1**;

FIG. **3** is a schematic illustration of the process for producing the composite article of FIG. **1**.

FIG. **4A** is an orthogonal top view of an exemplary composition of the composite article of FIG. **1**; and

FIG. **4B** is an orthogonal side sectional view of the composite article of FIG. **4A**.

DETAILED DESCRIPTION

The present invention includes a carbon-graphite/silicon carbide composite article. In the preferred embodiment, the composite article comprises a dense silicon carbide body; two interstitial regions: (1) a dense layer rich in silicon metal and (2) a small silicon carbide/silicon metal/carbon-graphite layer; and a carbon-graphite body. The microstructure of the carbon-graphite body is porous and can be impregnated with a variety of impregnants to further enhance the tribological-physical-chemical characteristics of the carbon-graphite body, or to eliminate the porosity for seal applications.

As can best be seen in FIGS. **1** and **2A–C**, in the preferred embodiment the composite article of the present invention comprises a carbon-graphite body **10** bonded to a dense silicon carbide body **12**. A transition/bonding region **14** joins the carbon-graphite body **10** to the silicon-carbide body **12**. The transition/bonding region **14** comprises a layer of silicon metal **16** and an area **18** which includes inclusions of silicon carbide **20**, silicon metal **22**, and carbon-graphite **24**. The silicon carbide **20** results from conversion of carbon-graphite and silicon metal during the bonding process. The carbon-graphite body **10** may also include a variety of impregnants, such as resins/polymers, metals, glasses or

other inorganic moieties or materials to improve the tribological or other characteristics of the body, or to eliminate porosity in the carbon-graphite body.

The process for producing the composite article of the present invention is shown schematically in FIG. 3. Manufacture of the composite article begins with separate production of the two individual bodies, the carbon-graphite body and the silicon carbide body, e.g. a reaction bonded silicon carbide body. The carbon-graphite body is manufactured in known manner by mixing fillers, such as carbons, graphites, inorganic additives and binders, having a particle size distribution that yields a moldable powder and a desired microstructure. The binders include coal tar pitch, petroleum pitch and/or resins. The mixture is then molded or compacted into a green body. After compaction, the green body is heated at an elevated temperature sufficient to carbonize the binder to yield a carbon-graphite body. The peak temperature must also be high enough to stabilize the body to minimize size changes during the subsequent bonding process. Any size change in the bonding process will cause deformation in the final product and possible weakening of the bond. The carbon-graphite body is then heat treated. The peak temperature can either be realized in the primary carbonization operation or in a subsequent heat treating process. Typically, the carbon-graphite body is then machined to produce a body with a desired size within allowable tolerances.

The silicon carbide body is manufactured in known manner. A reaction bonded silicon carbide body could, for example, be manufactured by mixing fillers (carbons, graphites, silicon carbide and temporary binders) having a particle size distribution that yields a moldable powder and desired microstructure. The body is then molded or compacted into a green body, which is then heated to carbonize the temporary binder to provide an intermediate strength to the body as well as to provide carbon for the subsequent bonding process. If necessary, the body can then be machined to a desired size within a desired tolerance.

The carbon-graphite body and the silicon carbide body are then assembled and reacted to intimately bond the carbon-graphite body to the silicon carbide body and to fully densify the silicon carbide body. The reaction process involves placing the assembled bodies onto a tray fitted with rails, together with elemental silicon metal which can rest between the rails, and heating the assembled bodies until the silicon becomes molten and wicks up the rails to infiltrate the assembly. While the silicon metal infiltrates the assembly, it reacts with the silicon carbide body. The metal also fills the interstitial space between the silicon carbide body and the carbon-graphite body and reacts slightly with the carbon-graphite body surface. This reaction forms a silicon carbide layer, with residual silicon metal existing between the bodies to bond them together after cooling.

Any silicon metal that wicks to the exterior of the carbon-graphite body can easily be removed later via machining. After removal of any such silicon carbide skin, the composite article may then be impregnated (using techniques common for porous carbon-graphite materials) either to eliminate the porosity in the carbon-graphite body or to improve the tribological or other characteristics of the body (or both). The composite body can then be further machined if necessary.

FIGS. 4A–B show an exemplary composite article in which a groove or race **28** has been machined in silicon carbide body **12** to accommodate carbon-graphite body **10**. Carbon-graphite body **10** may be inserted into race **28** after both bodies **10** and **12** have been individually baked, heat treated, and machined as necessary. After assembly, bodies **10** and **12** may be reacted together and bonded with a layer of silicon metal as described above. As shown in FIGS. 2A–C and 4A–B, it is important that the carbon-graphite body and the silicon carbide body overlap in cross-section to ensure adequate bonding and bond shear strength.

The following examples illustrate the invention using a reaction bonded silicon carbide body. It would be clear to a person skilled in the art that a pressureless sintered silicon carbide body could be used in like manner, providing that the pressureless sintered silicon carbide has sufficient porosity to wick up silicon metal as described above.

EXAMPLE I

A composite article of the present invention as shown in FIGS. 4A–B was prepared from a reaction bonded silicon carbide body having the properties summarized in Table I (after being reacted) and a carbon-graphite body having the properties summarized in Table II (after being baked).

TABLE I

Apparent Density, gm/cm^3	3.1
Flexural Strength, psi	40,000–4 pt.
Compressive Strength, psi	400,000
Modulus of Elasticity, psi	56×10^6
Porosity, % Volume	0.1
Permeability	Nil
Hardness, HK200	2300
Temperature Limit:	
Oxidizing Atmosphere, ° F.	2500
Neutral Atmosphere, ° F.	2500
Coefficient of Thermal Conductivity, BTU/hr. ft^2 – ° F./ft. (at 70° F.)	85
Coefficient of Thermal Expansion, μ-in/in ° F. (70 to 1500° F.)	2.5

TABLE II

Apparent Density, gm/cm^3	1.75
Flexural Strength, psi	9000
Hardness, Scleroscope	85
Specific Resistance, ohm/inch cube	0.0018
Ash, % Weight	8

After reaction as described earlier, a composite article of the present invention was produced.

EXAMPLE II

Another example of a composite article of the present invention as shown in FIGS. 4A–B was produced from a body of the reaction-bonded silicon carbide described in Table I (after being reacted) and a carbon-graphite body having the properties summarized in Table III (after being baked).

TABLE III

Apparent Density, gm/cm^3	1.76
Flexural Strength, psi	7000
Hardness, Scleroscope	71
Specific Resistance, ohm/inch cube	0.0012
Ash, % Weight	4.6

EXAMPLE III

Another sample of a composite article of the present invention as shown in FIGS. 4A–B was prepared from a

reaction-bonded silicon carbide body having the properties summarized in Table I (after being reacted) and a carbon-graphite body having the characteristics summarized in Table IV (after being baked).

TABLE IV

Apparent Density, gm/cm^3	1.65
Flexural Strength, psi	5000
Hardness, Scleroscope	55
Specific Resistance, ohm/inch cube	0.0015
Ash, % Weight	approx. 5

The above description is not intended to limit the present invention. Alternative embodiments are possible. Accordingly, the scope of the invention should be determined by the appended claims and their legal equivalence, not by the embodiments described and shown above.

What is claimed is:

1. A composite article comprising:

a. a first body comprising reaction bonded silicon carbide;

b. a second body of carbon-graphite; and

c. a transition region joining the first and second bodies, comprising a layer of silicon metal.

2. A composite article according to claim 1 in which the transition region includes an area comprising inclusions of carbon-graphite, silicon metal, and silicon carbide.

3. A composite article according to claim 1 in which the second body includes at least one impregnant.

4. A composite article according to claim 1 in which the transition region further includes an area comprising inclusions of carbon-graphite and silicon carbide.

5. A composite article according to claim 1 in which the second body includes at least one impregnant.

6. A composite article according to claim 2 in which the second body includes at least one impregnant.

7. A composite article according to claim 3 in which the second body includes at least one impregnant.

8. A composite article consisting essentially of:

a. a first body of reaction bonded silicon carbide;

b. a second body of carbon-graphite; and

c. a transition region joining the first and second bodies comprising a layer comprising silicon metal and a layer comprising silicon carbide, silicon metal, and carbon graphite.

9. A composite article consisting essentially of:

a. a first body of silicon carbide;

b. a second body of carbon-graphite;

c. a transition region joining the first and second bodies comprising a layer comprising silicon metal and a layer comprising silicon carbide, silicon metal, and carbon graphite; and

d. at least one inorganic impregnant.

10. A composite article comprising a carbon-graphite body partially embedded in a silicon carbide body and adhered thereto by a transition layer comprising silicon metal.

11. A composite article as claimed in claim 10 in which the transition layer further comprises a layer between the silicon metal and carbon-graphite, the layer being formed by reaction therebetween.

12. A composite article comprising a silicon carbide body partially embedded in a carbon-graphite body and adhered thereto by a transition layer comprising silicon metal.

13. A composite article as claimed in claim 12 in which the transition layer further comprises a layer between the silicon metal and carbon-graphite, the layer being formed by reaction therebetween.

14. A composite article comprising:

a. a first body comprising silicon carbide;

b. a second body of carbon-graphite; .

c. a transition region joining the first and second bodies comprising a layer comprising silicon metal and a layer comprising silicon carbide, silicon metal, and carbon graphite.

15. The composite article according to claim 14, wherein the silicon carbide of the first body is reaction bonded silicon carbide.

16. The composite article according to claim 14, wherein the second body further comprises at least one impregnant.

17. The composite article according to claim 14, wherein the transition region further comprises an area comprising inclusions of carbon-graphite and silicon carbide.

* * * * *

US006017633A

United States Patent [19]

Mercuri

[11] **Patent Number: 6,017,633**

[45] **Date of Patent: *Jan. 25, 2000**

[54] **FLEXIBLE GRAPHITE COMPOSITE SHEET AND METHOD**

[75] Inventor: **Robert Angelo Mercuri**, Seven Hills, Ohio

[73] Assignee: **UCAR Carbon Technology Corporation**, Danbury, Conn.

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: **08/887,188**

[22] Filed: **Jul. 2, 1997**

Related U.S. Application Data

[63] Continuation-in-part of application No. 08/819,744, Mar. 18, 1997.

[51] **Int. Cl.**[7] **B32B 9/00**

[52] **U.S. Cl.** **428/408**; 428/237; 428/323; 428/409; 428/411.1; 428/913; 428/920; 427/180; 423/448; 423/460; 264/113; 264/115

[58] **Field of Search** 428/913, 408, 428/323, 411.1, 920, 237, 409; 427/180; 264/113, 115; 423/449.3, 448, 460

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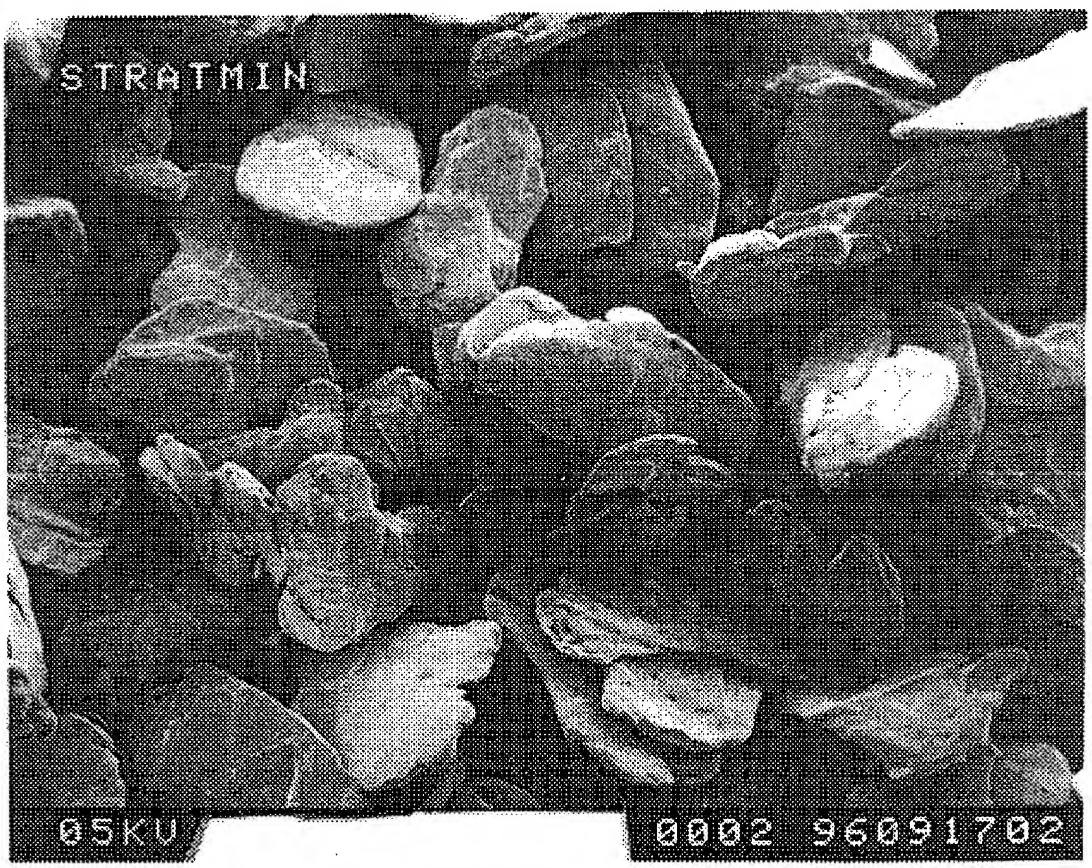
Primary Examiner—Deborah Jones
Assistant Examiner—Abraham Bahta
Attorney, Agent, or Firm—Frederick J. McCarthy

[57] **ABSTRACT**

Flexible graphite sheet is made by compressing a mixture of fine particle of intercalated, exfoliated, expanded natural graphite with fine particles of intercalated, unexpanded, expandable particles of natural graphite, the unexpanded particles being more finely sized than the expanded particles. The resulting sheet of flexible graphite exhibits improved fire retardant and sealability properties.

1 Claim, 4 Drawing Sheets



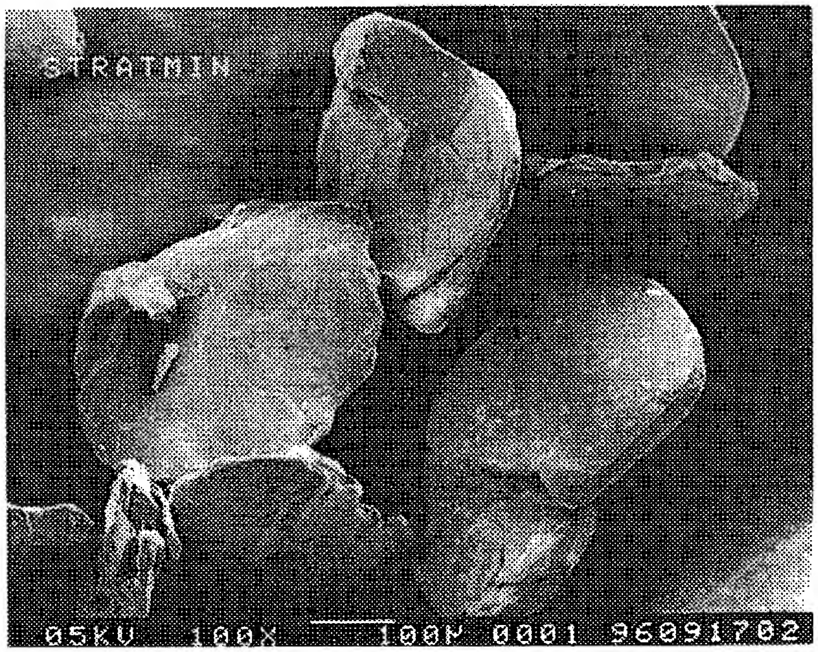

STRATMIN
05KV 100X 100P 0001 96091702

Fig. 1


STRATMIN
05KV 0002 96091702

Fig. 2

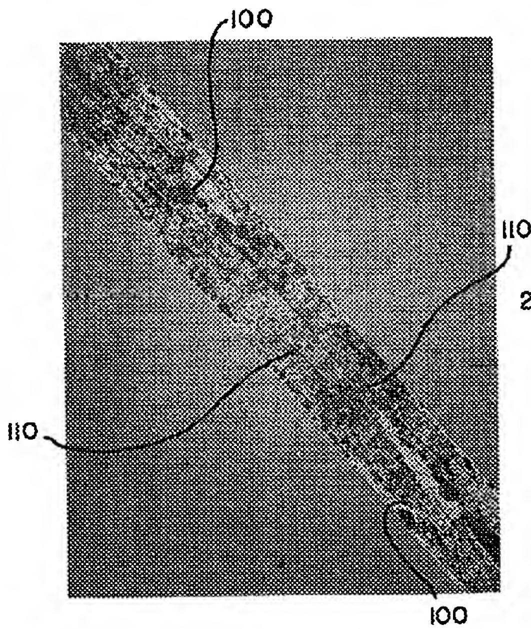


Fig. 3

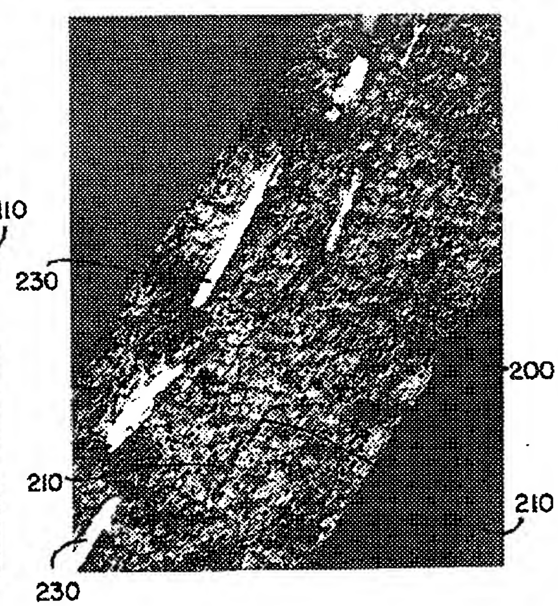


Fig. 4

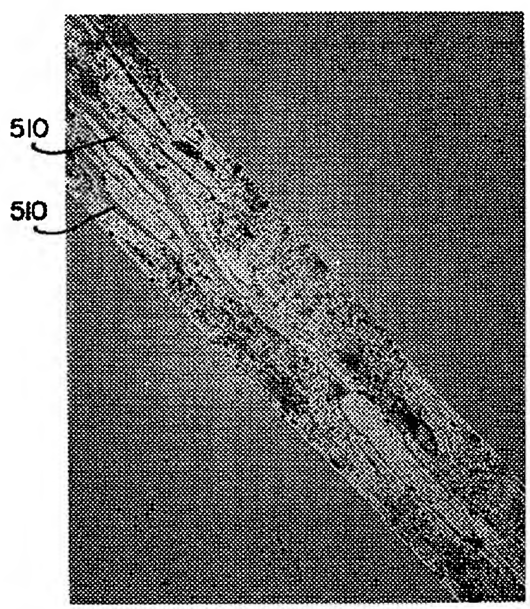


Fig. 5

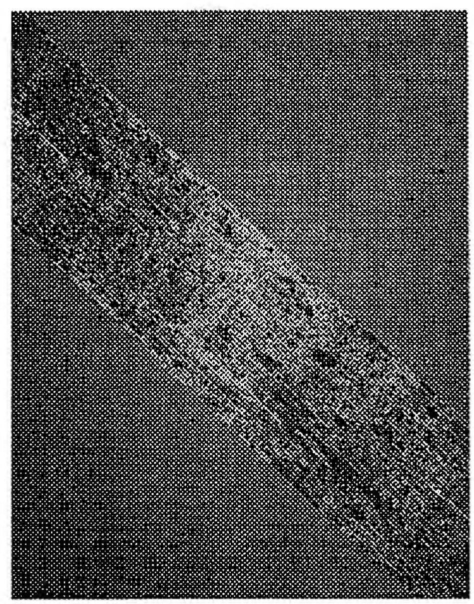


Fig. 6

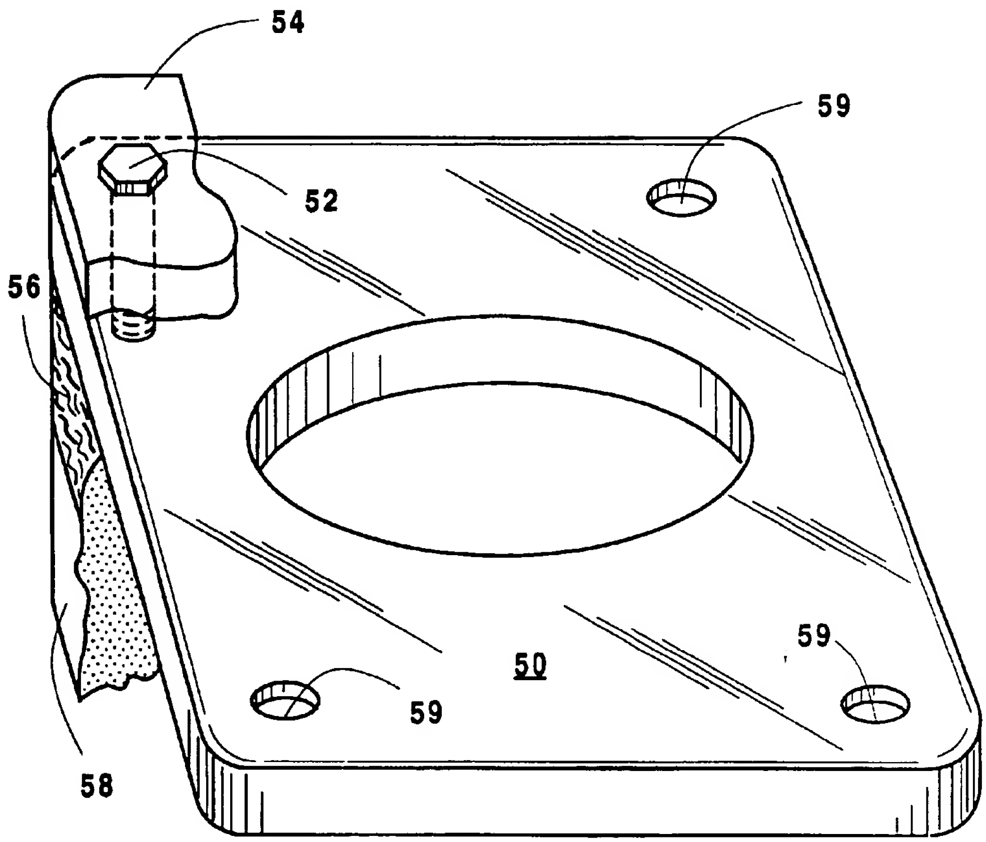


Fig. 7

FLEXIBLE GRAPHITE COMPOSITE SHEET AND METHOD

This application is a continuation-in-part of application Ser. No. 08/819,744 filed Mar. 18, 1997.

FIELD OF THE INVENTION

This invention relates to flexible graphite sheet which includes a heat expandable component to enhance fire retardance and the sealability of gaskets made from such sheet.

BACKGROUND OF THE INVENTION

Flexible graphite is commercially used in sheet form for the manufacture of gaskets. The flexible graphite sheet can be in the form of compressed exfoliated, expanded particles of graphite, or, in the form of a compressed mixture of exfoliated, expanded particles of graphite and unexfoliated, intercalated, unexpanded, expandable particles of graphite. This latter embodiment has the advantage of undergoing expansion while in place as a gasket upon exposure to high temperature so that sealing is enhanced. Material of this type has also been proposed for use as a fire retardant covering for walls and other flammable substitutes since expansion of the intercalated expandable graphite upon exposure to flame acts as a fire retardant. For commercial reasons it has become advantageous to use increasingly smaller sized natural graphite particles, i.e. small sized flake as the starting material in making such sheet material. With the use of such finer material the expansion and fire retardation effect of the sheet has become uneven largely on account of the tendency of the exfoliated expanded particles and the unexpanded intercalated particles to segregate and result in a non-homogeneous product with irregular sealing and fire-retardant behavior. This problem is avoided in the flexible graphite sheet material of the present invention by the use of differently sized batches of natural graphite flake as starting materials for the respective exfoliated and expandable components of the flexible graphite sheet to be used in the manufacture of gaskets or fire retardant substrate coverings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a scanning view electron microscope (SEM) at an original magnification of 100× showing natural graphite flake sized in the range of 20×50 mesh;

FIG. 2 is a scanning electron microscope (SEM) view at an original magnification of 100× showing natural graphite flake sized 50×80 mesh;

FIG. 3 and FIG. 6 are scanning electron microscope (SEM) views at an original magnification of 35× showing a flexible graphite sheet in accordance with the present invention;

FIGS. 4 and 5 are scanning electron microscope (SEM) views at an original magnification of 35× showing prior art flexible graphite sheet;

FIG. 7 shows a gasket in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Naturally occurring graphite is a crystalline form of carbon comprising atoms bonded in flat layered planes with weaker bonds between the planes. By treating particles of natural graphite with an intercalant of e.g., a solution of sulfuric and nitric acid, the crystal structure of the graphite

reacts to form a compound of graphite and the intercalant. Grinding, milling and other mechanical treatment of naturally occurring graphite can change the crystal orientation of graphite and the effectiveness of the intercalant. The treated intercalated particles of graphite are known as particles of "heat expandable graphite" and are commercially available. Upon exposure to high temperature, the particles of intercalated graphite undergo intumescence and expand in dimension as much as 80 or more times its original volume in an accordion-like fashion in the c-direction, i.e. in the direction perpendicular to the crystalline planes of the graphite. The exfoliated, i.e. expanded graphite particles are vermiform in appearance, and are therefore commonly referred to as worms.

A common method for making expandable graphite particles is described by Shane et al in U.S. Pat. No. 3,404,061 the disclosure of which is incorporated herein by reference. In the typical practice of this method, natural graphite flakes are intercalated by dispersing the flakes in a solution containing an oxidizing agent e.g., a mixture of nitric and sulfuric acid. The intercalation solution contains oxidizing and other intercalating agents known in the art. Examples include those containing oxidizing agents and oxidizing mixtures, such as solutions containing nitric acid, potassium chlorate, chromic acid, potassium permanganate, potassium chromate, potassium dichromate, perchloric acid, and the like, or mixtures, such as for example, concentrated nitric acid and chlorate, chromic acid and phosphoric acid, sulfuric acid and nitric acid, or mixtures of a strong organic acid, e.g. trifluoroacetic acid, and a strong oxidizing agent soluble in the organic acid.

A preferred intercalating agent is a solution of a mixture of sulfuric acid, or sulfuric acid and phosphoric acid, and an oxidizing agent, i.e. nitric acid, perchloric acid, chromic acid, potassium permanganate, hydrogen peroxide, iodic or periodic acids, or the like. Although less preferred, the intercalation solutions may contain metal halides such as ferric chloride, and ferric chloride mixed with sulfuric acid, or a halide, such as bromine as a solution of bromine and sulfuric acid or bromine in an organic solvent.

After the flakes are intercalated excess solution is drained from the flakes and after washing with water, the intercalated graphite flakes are dried and are expandable upon exposure to a flame for only a few seconds. Commercially available expandable graphite flake product is available from UCAR Carbon Company Inc.

The thus treated particles of graphite are hereafter referred to as "particles of intercalated graphite". Upon exposure to high temperature, the particles of intercalated graphite expand in dimension as much as 80 to 1000 or more times its original volume in an accordion-like fashion in the c-direction, i.e. in the direction perpendicular to the crystalline planes of the graphite. The exfoliated graphite particles are vermiform in appearance, and are therefore commonly referred to as worms. The worms may be compressed together into flexible sheets which, unlike the original graphite flakes, can be formed and cut into various shapes.

It is known to use a compressed sheet of combined exfoliated flexible graphite particles and unexfoliated, intercalated graphite particles in a gasket shape in a contacting gasket relationship and for use as a fire proof floor or wall covering. When used as a gasket, the gasket will expand upon contact with high temperature and also provide a gas tight fire proof seal. When used as a fire retardant wall covering the expansion of the intercalated graphite component on exposure to flame acts to extinguish the flame.

In a particular embodiment of the present invention, a first batch of relatively fine natural graphite flake particles, i.e. naturally occurring graphite flake, as shown in FIG. 1 (original magnification 100x), at least 80% by weight sized 20x50 mesh (through 20 mesh on 50 mesh), are treated by dispersing the naturally occurring flakes in an intercalating solution such as above-described. After the flakes of the first batch are intercalated, excess solution is drained from the flakes which are then washed with water and dried. The dried flakes of the first batch are exposed to a flame for only a few seconds and the intercalated flake particles expand, i.e. exfoliate, into vermicular, worm-like particles which are about 80 to 1000 times the volume of the initial dried intercalated flakes. A second batch of smaller sized natural graphite flakes as shown in FIG. 2 (original magnification 100x), sized at least 80% by weight 50 by 80 mesh (through 50 mesh on 80 mesh), is treated with an intercalating solution in the same manner as the first batch and similarly water-washed and dried. These unexfoliated intercalated natural graphite flakes, at least 80% by weight 50 by 80 mesh, are mixed and blended with the exfoliated particles of the first batch to provide from about 5% to 25% by weight of unexfoliated intercalated natural graphite flake in the mixture. The unexfoliated intercalated natural graphite flake particles are readily mixed with the high volume exfoliated, vermicular particles to provide a substantially uniform blend of unexfoliated, unexpanded flake and exfoliated, expanded vermicular particles. This can be achieved, for example, by spreading the finer, unexfoliated natural graphite particles over a bed of exfoliated natural graphite particles which are positioned on a vibrating table. The intercalated, unexfoliated particles of natural graphite are of a size which are substantially uniformly entrapped and surrounded in a contiguous matrix of exfoliated natural graphite particles which when roll-pressed, results in a flexible graphite sheet in which the intercalated, unexfoliated natural graphite particles **100** are substantially uniformly "locked" by compression in a matrix **110** of compressed exfoliated natural graphite as shown in FIG. **3**.

The use of finer than 80 mesh sized unexfoliated intercalated natural graphite flake has been found to result in a concentration of such particles near the surface of the bed of large exfoliated graphite particles. The finer particles are thus not uniformly entrapped in the mass of larger exfoliated particles resulting in a non-uniform final product material. The use of finer than a 80 mesh sized unexfoliated, intercalated graphite flakes also has been found to result in a flake with excess retained water content which results in a sheet which loses expansion capability and thus has a limited shelf life.

Larger sized, e.g. 30x50 mesh intercalated, unexfoliated natural graphite particles tend to agglomerate and result in non-uniformity in the mixture and the formation of disruptive channels during expansion when in use as a gasket or fire retardant covering.

EXAMPLE I (PRIOR ART)

Natural graphite flake, sized 80% by weight 20x50 mesh, (FIG. 1) was treated in a mixture of sulfuric (90 wt. %) and nitric acid (10 wt. %). The thus treated intercalated natural occurring flake was water washed and dried to about 1% by weight water. A portion of the treated, intercalated heat expandable natural graphite flake was introduced into a furnace at 2500° F. to obtain rapid expansion of the flake into one pound of vermicular, worm shaped particles having a volume of about 325 times that of the unexpanded intercalated flake. Treated, unexpanded intercalated natural graphite flake, in the amount of 0.18 pounds, was blended with the worm shaped, heat expanded graphite particles to provide a blended mixture containing about 15% by weight of unexpanded, intercalated natural graphite flake sized 20 by 50 mesh.

The blended mixture of worm shaped heat expanded, intercalated graphite flake with unexpanded graphite flake was rolled into a sheet about 0.060 inch thick and 12 inches in width. Samples of the sheet 0.060 inch thick shown in cross-section at 35x original magnification in FIG. **4** show the voids **200** and cracks **210** caused by relatively large flakes and the non-uniform distribution of the expandable, intercalated flakes **230**.

Large 8.5x11 inch sheets of Example I were heated in an oven to 250°, 300° and 400° C. The variation in thickness and density across a cross-section of the sheets is given in the Table below:

Heating Temp. (° C.)	Variation in Expansion (%)	Variation in Density (#/Ft.^{2})
250°	0–100	70–35
300°	100–500	35–4
400°	100–800	35–3

Sample of the sheet were cut to ½ IDx1 ¾" OD by 0.060" thickness and heated in a oven set at the temperatures.

The results of these tests showed that at 400° C. the samples are much more expanded on the one side vs. the other, i.e. approximately 2 times as much variation in expansion.

EXAMPLE II

The procedure of Example I was followed except that the thickness of the bed was reduced and attempts were made to roll the material into sheet about 0.020" thick. This effort was not sucessful as shown in FIG. **5**, due to the agglomeration and the concentration of material towards one side of the bed the material could not be calendared into a continuous sheet of uniform thickness as illustrated by voids **510**.

EXAMPLE III (This Invention)

A first batch of natural graphite flake, sized 80% by weight 20x50 mesh, (FIG. 1) was treated in a mixture of sulfuric (90 wt. %) and nitric acid (10 wt. %). The thus treated, intercalated natural graphite flake was water washed and dried to about 1% by weight water, a portion of the intercalated heat expandable natural graphite flake was introduced into a furnace at 2500° C. to obtain rapid expansion of the flake into one pound of vermicular, worm shaped particles having a volume of about 325 times that of the unexpanded intercalated flake.

A second batch of smaller sized natural graphite flake, sized 80% by weight 50x80 mesh (FIG. 2) was treated in a mixture of sulfuric and nitric acid and water washed in the same manner as the first batch of larger sized natural graphite to obtain intercalated, unexpanded heat expandable natural graphite flake.

A portion, consisting of 0.18 pounds of the intercalated, unexpanded, heat expandable natural graphite flake of the smaller particle sized second batch material was blended with one (1) pound of the worm shaped heat expanded particles of the first batch to provide a blended mixture containing about 15% by weight of unexpanded, intercalated natural graphite flake.

The mixture of worm shaped heat expanded natural graphite particles and unexpanded, intercalated natural graphite flake was rolled into a sheet about 0.050 inch thick and 24 inches in width.

Samples (8.5 inch×11 inch) of the sheet from this Example III were tested for expansion at 250°, 300° and 400° C.; the reduced variation, as compared to Example I, in expansion and density are shown in the following Table:

Heating Temp. (° C.)	Variation in Expansion (%)	Variation in Density (#/Ft.^{2})
250°	75–125	40–30
300°	400–600	14–10
400°	650–900	9–7

*Mesh sizes used herein are United States screen series.

EXAMPLE IV (This Invention)

The material of Example III was rolled into sheets about 0.015 inch and 0.020 inch thick, respectively. Both attempts were successful, resulting in satisfactory continuous sheet, thus demonstrating the importance of using the particle size of the present invention. A sample of the 0.015inch thickness sheet is shown in cross-section, at 35× original magnification, in FIG. 6. The sheet of FIG. 7, in accordance with the present invention is of uniform density and thickness and contains no acceptable voids or fissures.

EXAMPLE V

A test apparatus designed to use a gasket of the type shown in FIG. 7 was used to measure the ability of various graphite sheets (0.032 in. thick) in the form of a gasket as shown in FIG. 7, to seal a fixture and thus resist nitrogen flow. Three channels, each containing the identical shape and weight of material of exfoliated sheet and samples of Example 1 and Example 3 were heated to 400° C. After heating, the resistance to nitrogen flow of each of the sheets was measured at the same conditions of temperature and pressure. The results are shown below:

Type of Material	Relative Resistance to Flow
100% Exfoliated Graphite Sheet (Control)	0.0002
Example 1 (Prior Art)	0.0007
Example 3 (Present Invention)	10.000

Whereas, the seal of the Prior Art compared with the Control, improved by a factor of 3.5, the seal of the Present Invention is improved by 50,000 times compared to the Control due to the presence of finely sized intercalated unexfoliated graphite flake which expands at the higher temperature of 400° C. to tighten the seal.

Calendared material of the type of Example III 0.001 inch thick, containing 21% by weight needle shaped ceramic fibers was formed, by punching, into a gasket of the type shown at **56** in FIG. **7**, secured between metal plate **54** and metal block **58** by bolts **52** which pass through openings **59** in gasket **56**.

What is claimed is:

1. A sealing gasket formed of a flexible graphite roll-pressed sheet of a blended mixture of (i) exfoliated expanded natural graphite particles formed of heat expanded intercalated natural graphite flake sized at least 80% by weight 20 by 50 mesh prior to heat expansion and (ii) unexfoliated intercalated natural graphite flake sized at least 80% by weight 50×80 mesh, the amount of the unexfoliated intercalated natural graphite flake in the blended mixture and in the flexible sheet being from 5 to 25% by weight and said unexfoliated intercalated natural graphite flake being uniformly entrapped and surrounded in a continuous matrix of exfoliated natural graphite particles.

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